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Mechanisms of the Reaction of Diborane with Silica Gels and Silicoalumina Hydroxylic Surfaces

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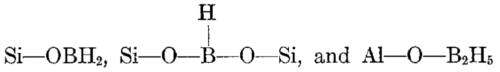
Reaction mechanisms of diborane with hydroxylic surfaces of several silica gels, characterized by different pore radii, and of a silicoalumina, have been studied by means of hydrolysis ratios, infrared spectroscopy of adsorbed species, and reaction kinetics. The reaction is preceded by an induction period which has been interpreted by the dissociation of B_2H_6 into BH_3 groups and the adsorption of BH_3, reacting as Lewis acids with surface oxygen atoms. BH_2 and BH radicals linked to oxygen atoms are formed by reactions of BH_3 with surface water as well as with hydroxyls. Hydrolysis ratios appear to be >2 for hydration water and $\leqslant 2$ for silanols. A single kinetic mechanism seems to operate, irrespective of the water or hydroxyl surface density, above a limit of 1.4 mobile H surface atoms per 100 Å^2. The limiting rate process is probably the dissociation of B_2H_6 into BH_3, which is required for maintaining an adequate concentration of BH_3 groups around surface hydroxyls and hydration water molecules.

INTRODUCTION

Numerous techniques have been proposed for determining the surface hydroxylic content of silicates. Hydration water and hydroxyl groups contribute to the surface content in varying proportions according to the pretreatment temperature. Several papers dealing with distinction between the two components have been published. Hydrolysis of diborane has been used for this purpose; the ratio of the number of hydrogen molecules produced to the number of diborane molecules consumed by the reaction appears to be different for hydration water and for surface hydroxyl groups.* According to Weiss, Knight, and Shapiro (*1–4*) the hydrolysis ratio of adsorbed water is 6 regardless of the reaction temperature, while the hydrolysis ratio of surface-bound hydroxyls is temperature-dependent and changes from 2 to 4 between —23° and 100°C. With respect to hydrolysis ratios, the behaviors of silica gels and of silicoaluminas with composition in the 15% Al_2O_3 range do not differ so long as the pretreatment temperature remains lower than 250°C. By assuming that boron isotopic exchange occurs if a boron atom is linked to the surface by only one oxygen atom, Weiss *et al.* postulated the existence of the following surface radicals:



$$Si{-}OBH_2,\ Si{-}O{-}\overset{H}{\overset{|}{B}}{-}O{-}Si,\ \text{and}\ Al{-}O{-}B_2H_5$$

Naccache and Imelik (*5–7*) arrived at rather different conclusions. In silica gels, the hydrolysis ratios of B_2H_6 with hydration water and hydroxyls are 2 and 1, respectively, the reactions being those shown at the top of the next page. Moreover Mathieu (*8*) and Mathieu and Imelik (*9*) have checked these reaction paths by infrared spectroscopy in the BH stretching region: They observed that the reaction with hydration water produced radicals characterized by rather simple

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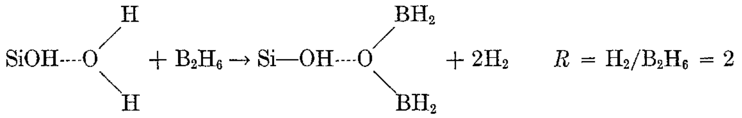
*In this paper, hydration water means adsorbed molecular water, and surface hydroxyls or radicals, constitution OH groups linked to Al or Si near the surface.



$$\mathrm{SiOH{\cdots}O(H)_2 + B_2H_6 \rightarrow Si{-}OH{\cdots}O(BH_2)_2 + 2H_2} \qquad R = H_2/B_2H_6 = 2$$

$$\mathrm{Si{-}OH + B_2H_6 \rightarrow Si{-}O{-}B_2H_5 + H_2} \qquad R = 1$$

B–H bands with a sharp component at 2580 cm^{-1} and two shoulders at 2600 cm^{-1} and 2510 cm^{-1}. The band at 2580 cm^{-1} was attributed to asymmetrical stretching of BH_2 and the weaker band at 2510 cm^{-1} to the symmetrical BH stretching. These surface radicals were thermally unstable and disappeared gradually on heating above 50°C. Reactions with silanols produced radicals characterized by an intense band at 2560 cm^{-1} and a doublet at 2465 cm^{-1} and 2440 cm^{-1}. These bands still appeared in samples heated under vacuum at 300°C. The intense component was attributed to asymmetrical stretching and the doublet to two symmetrical vibrations.

Considering the discrepancies between the conceptions of Weiss *et al.* and Imelik and his collaborators, the present study was devoted mainly to the reaction mechanism of diborane with hydroxylic surfaces.* Hydrolysis ratios have been measured, the infrared spectra of chemisorbed species have been observed, and the reaction kinetics has been studied.

As the reaction of a gas with an active solid surface is relevant to catalytic phenomena, results of this study are of more general interest than work restricted to the analysis of hydroxylic surfaces.

PROCEDURES

a. Materials and reagents. Silica gels were prepared by precipitation from a sodium silicate solution (Merck, density 1.36) through addition of formol as proposed by Imelik and Carteret (*10*).

The differentiation of Aerogel and Xerogel is founded mainly on texture, Aerogel having a larger average pore radius than Xerogel. This probably arises from a higher precipitation rate for Aerogel, due to the use of more concentrated silicate solutions.

The preparation procedures, the texture characteristics and the main impurity contents are indicated in Table 1. Silico-

TABLE 1

PREPARATION PROCEDURE, SPECIFIC SURFACE AREA (S_0), AND IMPURITY CONTENTS

Sample	Preparation	Impurity (g ion/g SiO_2)	S_0 (m^2g^{-1}) (at 100°C)	Average pore radius (Å)
Xerogel	100 ml Na silicate + 1400 ml H_2O + 1500 ml formol[a]	3.2×10^{-6} Na^+	410	35
Aerogel I	400 ml Na silicate + 1100 ml H_2O + 1500 ml formol[a]	0.86×10^{-6} Na^+	220	120
Aerogel II	600 ml Na silicate + 900 ml H_2O + 1500 ml formol[a]	6.25×10^{-6} Na^+	135	~400
Silicoalumina (13% Al_2O_3)	—	145×10^{-6} NH_4^+	538	24

[a] Purified by refluxing with *N* HCl, followed by washing with water.

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* Note added during review: An interesting study on the interaction of B_2H_6 with silica gels has been published quite recently by Baverez and Bastick (*29*). From isotopic exchange and infrared spectroscopy results, these authors have shown that B_2H_6 reacts simultaneously with surface hydroxyls and with oxygen atoms of siloxane bridges. Moreover they conclude also that the diborane method does not permit the distinction between hydration water and silanols. References to this work have been added to the present manuscript in several places.

TABLE 2

Surface Hydroxyls, Hydration Water Molecules, and Total Hydroxyl Content[a]

Outgassing temperature (under vacuum) (°C)	Surface hydroxyl groups	Hydration water molecules	Total hydroxyl content[b]	Surface hydroxyl groups	Hydration water molecules	Total hydroxyl contents[b]
		Aerogel II			Aerogel I	
50°	0.37	1.05	3.22	1.6	0.35	5.05
100°	0.45	0.94	3.00	1.6	0.26	4.85
150°	0.55	0.79	2.68	1.6	0.16	4.64
200°	0.63	0.63	2.35	1.56	0.07	4.32
250°	0.70	0.45	2.04	1.52	0.0	3.94
300°	0.76	0.27	1.64	1.42	—	3.42
400°	0.77	—	1.85	1.18	—	2.30
500°	0.45	—	0.45	1.00	—	1.44
600°	0.32	—	0.32	0.8	—	0.84
700°	0.29	—	0.22	0.7	—	0.74
		Xerogel			Silicoalumina	
50°	1.52	1.28	5.12	7.2	4.2 − 3.5	15.8
100°	1.80	1.0	4.84	6.5	3.1 − 2.6	13.0
150°	2.1	0.68	4.00	5.6	2.5 − 1.8	10.8
200°	2.3	0.35	3.18	4.4	1.9 − 1.1	9.3
250°	2.36	0.14	2.64	3.5	1.4 − 0.6	7.4
300°	2.27	0.0	2.30	2.8	1.1 − 0.2	6.3
400°	1.80	—	1.80	1.7	0.9 − 0.0	4.0
500°	1.32	—	1.34	—	—	2.4
600°	0.90	—	0.88	—	—	1.2
700°	0.52	—	0.50	—	—	0.8

[a] 10^{-3} moles g^{-1}.

[b] Including surface, internal hydrolysis, and hydration water (counted for two OH groups) and determined by the weight loss after long heating in vacuum at 900°C.

alumina was kindly provided by Ketjen Zwavelzuur Fabriek N. V. (Netherlands).

The hydroxylic contents of the gels were determined according to the technique proposed by Fripiat and Uytterhoeven (*11, 12*) and are shown in Table 2. A comparison between these results and the amounts of hydroxyls reacting with diborane has been published elsewhere (*13*). In that paper (*13*), the unexpected increase of the amount of surface hydroxyls with outgassing temperature in Aerogel II and Xerogel has been particularly and is attributed to the presence of very fine pores occluded with hydration water. At higher temperature, these hydration molecules were removed progressively, leaving a more extended hydroxylic surface.

Diborane was produced in ether solutions by allowing $LiAlH_4$ to react with BF_3 under a N_2 atmosphere as proposed by Shapiro *et al.* (*14*). The gas was purified by low-temperature distillation. Analysis of the gas by mass spectrography disclosed traces of ether, and indicated moreover that diborane which had been brought in contact with silica gel and silicoalumina for more than 100 hr was not polymerized.

b. Hydrolysis ratio determinations. Determinations of hydrolysis ratios were carried out in classical volumetric apparatus in which the samples were pretreated under vacuum for at least 15 hr at temperatures ranging between 20° and 700°C. A known volume of diborane was introduced and allowed to react for 100 hr. The amount of H_2 evolved was measured by condensing B_2H_6. The *primary hydrolysis* ratio was determined by comparison of the volume of H_2 produced to the volume of B_2H_6 consumed. The sample was then carefully outgassed overnight at 25°C and

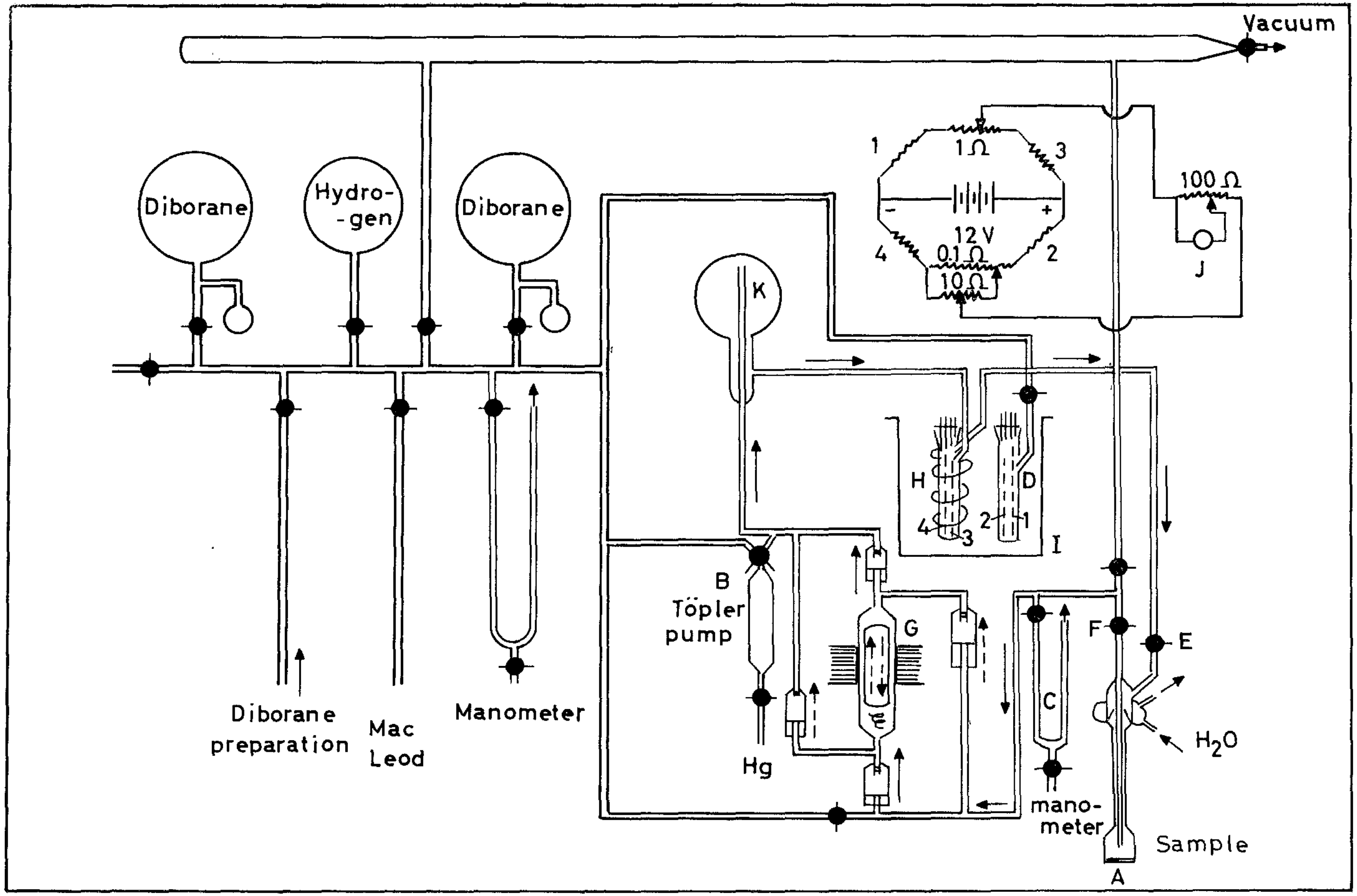


FIG. 1. Apparatus used for kinetics. H and D, two catharometers, each of them fitted with two platinum wires (1.2 and 3.4) connected as shown above; J. 0–25 mV recorder. G, circulation pump.

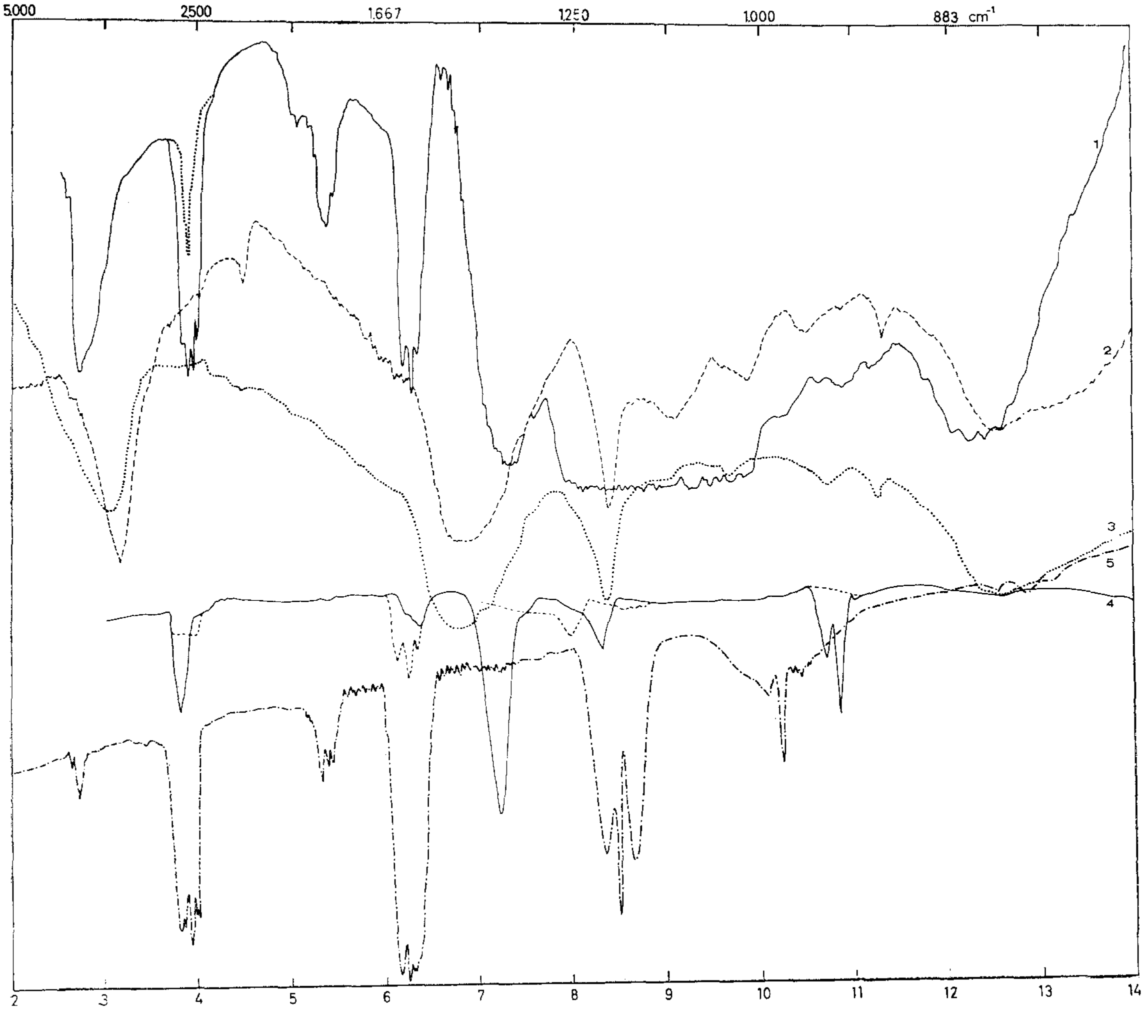


FIG. 2. Reference spectra 1, B_2H_6 in contact for 5 hr with Aerogel I pretreated at 150°C; gas pressure: 5 mm Hg; dotted line: BH band observed after B_2H_6 removal; 2, metaboric acid (in KBr, 2%); 3, boric acid H_3BO_3 (in KBr, 2%); 4, spectra given by Shalette and Porter (*23*). Boroxine obtained from the decomposition of pentaborane; solid line: 2 min after the explosion; dotted line: 1 hr after the explosion; 5, Gaseous B_2H_6; pressure: 40 mm Hg; optical path: 120 mm.

water vapor was introduced to the reaction cell in order to hydrolyze the surface radicals; the amount of H_2 produced was measured again and the *secondary hydrolysis* ratio was determined as the ratio of H_2 evolved in the second step to the volume of diborane consumed in the first one. The sum of both hydrolysis ratios must be equal to 6 if the procedures are applied correctly.

c. Kinetics. The reaction rate processes were followed with the apparatus shown in Fig. 1. H_2 was detected by catharometers made from two platinum wires arranged in a "crossed bridge" as proposed by Fripiat and Gastuche (*15*). A known volume of diborane was introduced through the Töpler pump B and allowed to circulate in the reaction cell A, by means of magnetic circulation pump G (flow rate ~0.2 mole 10^{-3} sec^{-1}). Pure B_2H_6 was isolated in catharometer D at the beginning of the run. The bridge response is standardized with known B_2H_6–H_2 mixtures.

d. Infrared spectroscopy. The reaction cell A (Fig. 1) was replaced by the in-

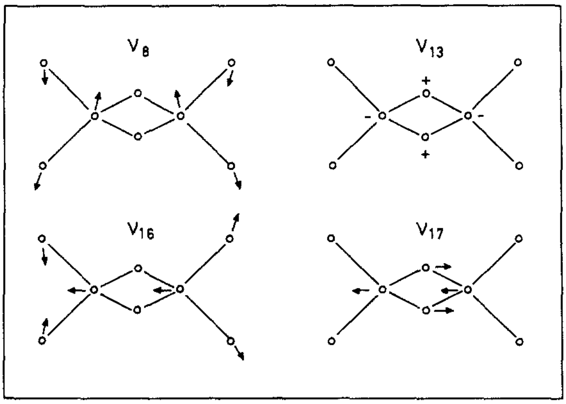
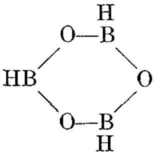


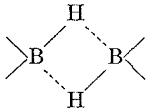
FIG. 3. ν_8, ν_{13}, ν_{16}, and ν_{17} normal modes of vibration of B_2H_6 according to Nakamoto (*16*).

frared cell designed by Fripiat, Gastuche, and Brichard (*16*) and the spectra were recorded between 2 and 8 μ with a Beckman IR4 spectrophotometer fitted with CaF_2 optics. In hydrolysis ratio determinations and in kinetics experiments powdered samples were used, while for infrared spectroscopy films were prepared by pressing the powder (*16*).

Figure 2 shows reference spectra which are of interest for this work while Table 4 will attempt to make the paper more readable by comparing the frequencies of the "reference" bands and the bands appearing in the materials in contact with diborane. According to Nakamoto (*17*), B_2H_6 belongs to the symmetry group V_h and is characterized by eight fundamental infrared active bands. Figure 3 shows the normal modes which do not interfere with Si–O bands. H_3BO_3 is a triangular coplanar molecule, the triangles being linked to each other by hydrogen bonds so that the symmetry group is C_{6h}. B–O stretching appears at 1490 cm^{-1}, according to Hornig and Plumb (*18*) and Servoss and Clark (*19*) or at 1450 cm^{-1}, according to Bettell and Sheppard (*20*). HBO_2 has been studied in the gaseous as well as in the solid state by White *et al.* (*21*): The molecule is linear but the hydrogen atom is tilted away from the O–B-O axis. B-O stretching is observed in HBO_2 at 2030 cm^{-1} or at 2260 cm^{-1} in the gas and solid phases, respectively, while the B–O stretching accordingly appears at 1420 cm^{-1} and 1470 cm^{-1}. In B_2O_3 (White and Walsh, *22*), in borates (Duval and Lecompte, *23*) and in boroxine,



(Shalette and Porter, *24*; Lee, *25*), the B–O stretching frequency is always lower than in hydroxylic compounds such as boric or metaboric acids. In boroxine, for example, B–O stretching is found at 1370 cm^{-1} (Fig. 2). This remark is very important since the frequency at which the B–O band will appear in the partial hydrolysis of diborane on hydroxylic surfaces will allow one to decide whether B–O–H bonds are or are not formed. The observation of the spectral region where the ν_{17} band of diborane appears (1606 cm^{-1}, see Fig. 3) is also of interest since this band characterizes the bridged



structure. If radicals such as B_2H_5 exist on the surface this band should be observed readily. It seems unlikely that the linkage of B_2H_5 with the surface through an oxygen atom could affect seriously its frequency since according to Lehmann *et al.* (*26*) it still appears in polymethyl diborane.

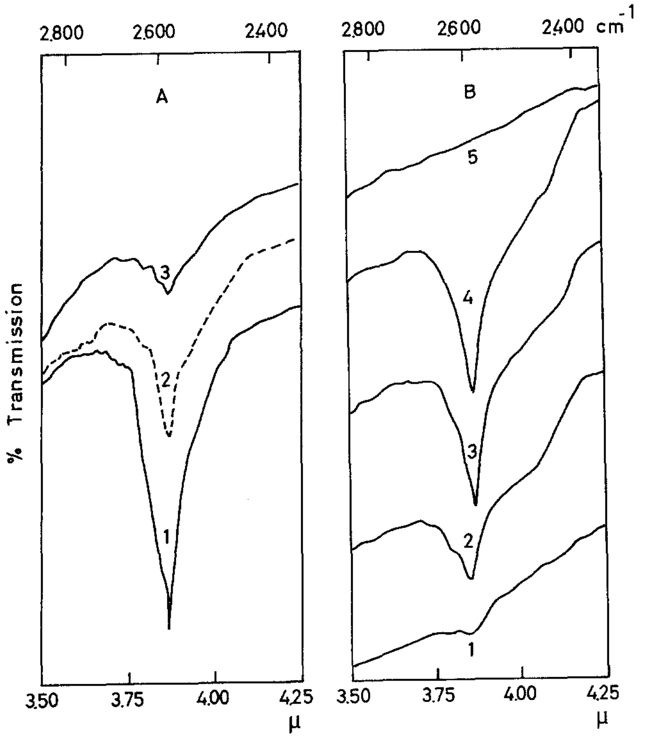


FIG. 4. A. Reaction of Aerogel I (pretreated under vacuum at 330°C) with B_2H_6 at 30°C (gas pressure, 50 mm Hg): 1, after 5 hr, sample outgassed at 30°C; 2, after partial hydrolysis of BH and BH_2 radicals by water vapor; 3, after almost complete hydrolysis.

B. Reaction of Aerogel I (pretreated under vacuum at 180°C) with B_2H_6 at 30°C (gas pressure, 50 mm Hg): 5, untreated sample; 4, after 4 hr, sample outgassed at 80°C; 3, sample outgassed at 140°C, 2, 190°C and 1, 250°C.

EXPERIMENTAL RESULTS

A. Hydrolysis Ratios

The primary and secondary hydrolysis ratios are shown in Table 3. The sum of both ratios was almost always slightly lower than 6 (in average 5.78). Primary hydrolysis ratios obtained for silica gels were always higher than 2 for pretreatment processes carried out at temperatures lower than 400°C, and approached unity in substances outgassed at temperatures higher than 600°C. These values are in good agreement with those proposed by Baverez and Bastick (*29*). For unknown reasons, Naccache and Imelik (*5–7*) did not find primary hydrolysis ratios noticeably higher than 2.

In the silicoalumina, the primary hydrolysis ratio decreased more rapidly with increasing outgassing temperature. Since the last traces of hydration water disappeared in silica gels between 300° and 400°C (Table 2), it may be concluded that hydrolysis ratios higher than 2 are in some way connected with the presence of this surface component. It must also be pointed out that a hydrolysis ratio equal to 3.85 was found for a high-surface-area gibbsite (80 m^2g^{-1}), outgassed under conditions such that hydration water had left the surface. This is an indication that Al–OH surfaces react differently from silanol surfaces.

B. Infrared Spectroscopy Results

Regardless of the pretreatment temperature and of the nature of the sample, two bands appeared clearly when silica gel films were exposed to diborane and than outgassed at 30–50°C for 1 hr approxi-

TABLE 3
PRIMARY AND SECONDARY HYDROLYSIS RATIOS
(MEASURED AT 25°C)

Sample	Pretreatment temperature (under vacuum)	Hydrolysis ratios		
		Primary reaction	Secondary reaction	Sum
Aerogel	40	2.6	—	—
	125	2.73	3.12	5.85
	200	2.54	3.06	5.6
	400	2.00	3.38	5.38
	600	1.41	4.48	5.89
Aerogel II	24	3.15	2.74	5.89
	135	2.69	3.24	5.93
	350	2.00	3.98	5.98
	640	1.15	4.18	5.33
Xerogel	100	2.50	3.33	5.83
	260	2.28	3.49	5.77
	411	2.07	4.01	6.08
	580	1.41	4.18	5.59
Silicoalumina	110	2.78	3.15	5.93
	275	1.78	4.10	5.88
	350	1.66	4.27	5.93
	650	0.99	4.73	5.93
	660	0.97	—	—
			Average:	5.78

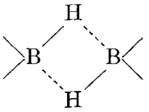
mately. These bands can be assigned to B–O and B–H stretchings and have frequencies very close to that in boroxine. Figures 4 and 5 show some examples of infrared spectra obtained under different conditions. In Table 4, the frequencies of the observed vibration bands are compared with reference data.

The B–H band is composed of a rather sharp and intense peak at 2580 cm^{-1}, with two weaker spectral components at 2600 and 2530 cm^{-1}. The BH band disappeared immediately on introducing water vapor into the cell, but its intensity also decreased on heating under vacuum. This is an indication of a possible migration of internal hydroxyls towards the surface. The BO band at 1375 cm^{-1} developed during the reaction of silica gels with B_2H_6 shifted to a higher frequency (~ 1430 cm^{-1}) during the secondary hydrolysis process when water vapor was allowed in the cell. This indicates that the B–O bond formed during the primary hydrolysis process is not hydrogen-bonded and that no B–OH linkage is formed in this step. On the contrary, hydrolysis of surface radicals by an excess of water vapor was followed by the formation of B–OH bonds.

For the silicoalumina outgassed at temperatures higher than 400°C, the results were identical to those observed for silica gels. At pretreatment temperatures lower than 200°C, the BH band was present in the form of two equally intense components at 2625 and 2585 cm^{-1}. Moreover, at the first stages of the reaction, transient bands at 2065, 800, and 1172 cm^{-1} were observed: This suggests the intermediate formation of HBO_2 and perhaps H_3BO_3.

As shown by Table 4 A, several discrepancies arise when comparing our data with those published by Mathieu and Imelik (*9*) or by Baverez and Bastick (*29*).

(1) With the outgassing procedure adopted here (1 hr approximately at 30–50°C), we have never observed bands which clearly suggest the presence of physically adsorbed B_2H_6: The shoulders at 2600 and 2530 cm^{-1} still being present after outgassing for 1 hr at 190°C (Fig. 4B), they obviously cannot be attributed to physically adsorbed species. In no instance either for silica gels or for silicoalumina, was the intense band around 1600 cm^{-1} due to the bridged



structure observed.

(2) In agreement with Baverez and Bastick but in contradiction with Mathieu and Imelik, the spectral features attributed to surface radicals were independent of the hydrolysis ratios, i.e., of the pretreatment temperature.

In connection with the interpretation of the infrared spectra, it is pertinent to note that

(a) Because of possible hydrogen bonding of the surface radicals (BH_2 or BH_3) with neighboring oxygens and of possible electron transfer from the surface, attempting frequency attributions from a too close

TABLE 4

A. Attribution of the Infrared Bands Observed between 2700-1300 cm^{-1} for Surface Radicals and Adsorbed Species. Relative Intensity: (s): Strong; (m): Medium; (sh): Shoulder; (Trans.): Transient Band; (d): Doublet

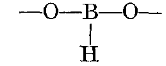
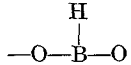
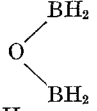
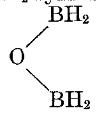
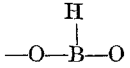
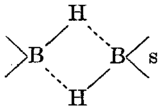
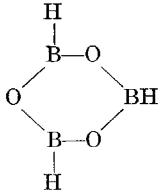
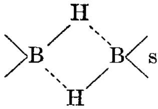
		Mathieu and Imelik (9) (Silica gels)		Baverez and Bastick (29) (Silica gels)		This work	
		Frequency (cm^{-1})	Attribution	Frequency (cm^{-1})	Attribution	Frequency (cm^{-1})	Attribution
SURFACE RADICALS		$R = 1$		Regardless of the R value		Silica gel: $1 < R < 2.7$ Silicoalumina: $R < 2$	
		2560 (s)	B—H asym. stretch. of $-\mathrm{O}-\mathrm{B_2H_5}$	2580 (s)	BH stretch. of  $-\mathrm{O}-\underset{\mathrm{H}}{\underset{\vert}{\mathrm{B}}}-\mathrm{O}-$	2600 (sh) 2580 (s)	BH stretch. of  $-\mathrm{O}-\overset{\mathrm{H}}{\overset{\vert}{\mathrm{B}}}-\mathrm{O}$ and $-\mathrm{O}-\mathrm{BH_2}$ asym. stretch. (see text)
		2465 (d, m)	B—H sym. stretch. of $-\mathrm{O}-\mathrm{B_2H_5}$			2530 (sh)	$-\mathrm{O}-\mathrm{BH_2}$ sym. stretch.
				1375	B—O stretch.	1375 (s)	B—O stretch.
		$1.5 < R \leq 2$				Silicoalumina: $R > 2$	
		2580 (s)	$\mathrm{BH_2}$ asym. stretch. of 			2625 (m)	$-\mathrm{O}-\mathrm{BH_2}$ asym. stretch.
		2510 (m)	$\mathrm{BH_2}$ sym. stretch. of 			2585 (s)	BH stretch. of  $-\mathrm{O}-\overset{\mathrm{H}}{\overset{\vert}{\mathrm{B}}}-\mathrm{O}$
						2065 (trans.) 1375 (s)	B=O stretch. of $\mathrm{HBO_2}$ B—O stretch.
ADSORBED SPECIES	$\mathrm{B_2H_6}$	2635 (m) 2515 (m)	Terminal $\mathrm{BH_2}$ stretch. Terminal $\mathrm{BH_2}$ stretch.	2597 (s) 2520 (m)	$\mathrm{BH_2}$ asym. stretch. $\mathrm{BH_2}$ sym. stretch.		
				2110–2090 (d) 1560–1535 (d)	 stretch.		
	$\mathrm{BH_3}$			2560 (s) 2479–2452 (d)	B—H stretch.		

TABLE 4

B. REFERENCE SPECTRA IN THE RANGE 2700–1300 cm^{-1} (SEE TEXT)

Gaseous B_2H_6		Gaseous HBO_2		Boroxine: 	
Frequency (cm^{-1})	Attribution	Frequency (cm^{-1})	Attribution	Frequency (cm^{-1})	Attribution
2612 2525	Terminal BH_2 stretch.	3680 2030	OH stretch. B═O stretch.	2585 1370	BH stretch. BO stretch.
1925 1606	 stretch.	1420	B—O stretch.		

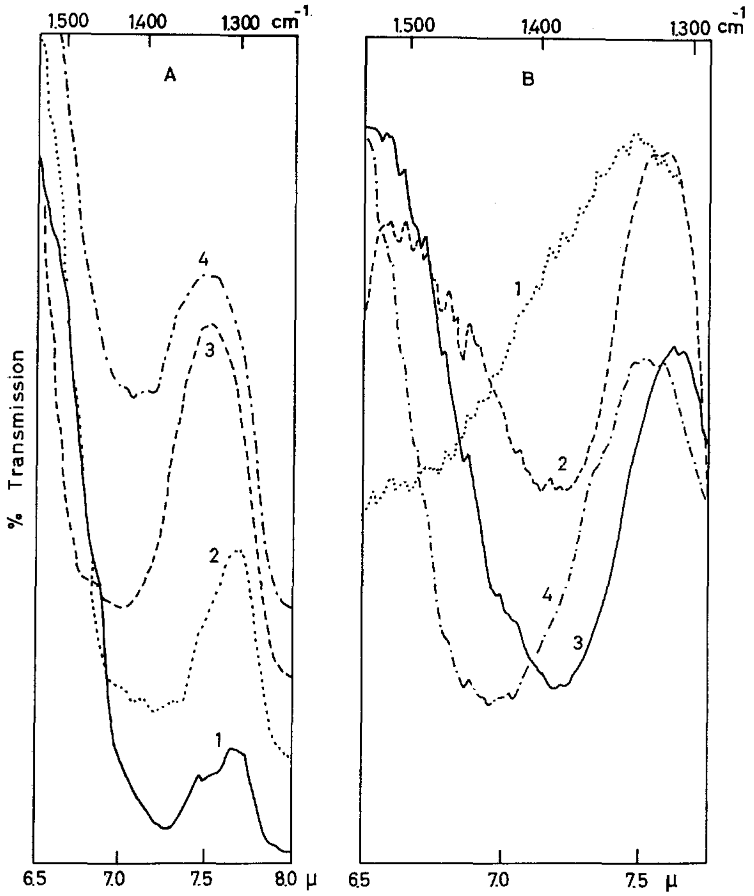
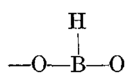


FIG. 5. A. BO stretching band observed during the reaction at 30°C of Aerogel I (pretreated at 150°C) with B_2H_6 (50 mm Hg): 1, after 5 hr: 2 and 3, after progressive introduction of water vapor; 4, after complete hydrolysis of BH radicals.

B. BO stretching band observed during the reaction at 30°C of silicoalumina (pretreated at 425°C) with B_2H_6 (50 mm Hg): 1, untreated sample; 2, after 30 min; 3, after 2 hr; 4, after complete hydrolysis by water vapor.

comparison with gaseous B_2H_6 is rather hazardous. If the 2580-cm^{-1} band seems doubtless to be relevant, at least partially, to BH stretching of



$$\overset{\displaystyle H}{\underset{}{-O-\overset{|}{B}-O}}$$

the weaker bands at 2600 or 2530 cm^{-1} might be attributed either to $-BH_2$ or to BH_3; however BH_3 could also contribute to the 2580-cm^{-1} band. In our opinion, the wavenumber domain between 2600 cm^{-1} and 2580 cm^{-1} is too narrow to ascertain more precise attribution.

(b) The doublet observed by Mathieu and Imelik at 2465–2440 cm^{-1} and by Baverez and Bastick at 2479–2452 cm^{-1} may have a rather ambiguous meaning; because of the strong CO_2 absorption in this frequency range the electronic balance of a double-beam instruments is always critical when working with poorly transmitting materials.

C. *Kinetics*

Kinetic experiments were always performed in the presence of an excess of diborane so that the apparent reaction order with respect to the gaseous reagent would be zero. The recorder deflection indicating the presence of H_2 mixed with B_2H_6 in the detector was always delayed for a variable time after the opening of the reaction cell. Calculations and blank experiments performed by injection of H_2 in B_2H_6, show that this "dead time" cannot be accounted for by the inertia of the detector response to the composition of the circulating gases.

It may therefore be accepted that the reaction was preceded by an "induction period" after which the reaction started very rapidly. The induction time appeared larger for both hydrated and completely dehydrated samples, with the minimum observed for samples pretreated between approximately 100° and 400°C (Table 5) but no appreciable differences were noted between gels characterized by different textures. It was also observed that the induction time increases markedly with the B_2H_6 pressure: For Aerogel I, for instance, it rises from approximately 5 min for a 0.2-g sample outgassed at 200°C, to 30 min when the B_2H_6 pressure goes from 50 mm to 100 mm Hg.

TABLE 5

INDUCTION PERIOD OBSERVED FOR AEROGEL I AS A FUNCTION OF THE PRETREATMENT TEMPERATURE[a]

Reaction temperature (°C)	Pretreatment temperature (°C)	Induction period (min)
0°	66°	7
	202°	5
	256°	7
	384°	7
	510°	11
20°	25°	31
	25°	44
	75°	3
	110°	2
	160°	2
	175°	5
	250°	3
	295°	3
	340°	3
	355°	7
	373°	3
	455°	5
	555°	37
	628°	22
40°	86°	5
	182°	3
	266°	4
	384°	8
	395°	7
	405°	5
	474°	5
	545°	13
	645°	24

[a] Sample weight, ~0.2 g; B_2H_6 pressure, 50 mm Hg.

After this induction period and as shown in Figs. 6 and 7, the rate process expressed in reduced coordinates, obeys well the empirical law

$$\alpha = \tau/(\tau + 0.25) \qquad (1)$$

where α is the advancement degree of the reaction and τ the reduced time $t/t_{0.8}$; the time t is considered from the end of the induction period while $t_{0.8}$ is the time necessary to reach $\alpha = 0.8$. The α is measured as the ratio of n_t, the number of H_2 molecules evolved at the time t, to n_∞, the number of H_2 molecules evolved for $t \rightarrow \infty$. Relationship (1) results from the integration of

$$d\alpha/d\tau = 4(1 - \alpha)^2 \qquad (2)$$

whence the reaction rate $(dn_t/dt)t_{0.8} = V^*$ at the time $t_{0.8}$ may be calculated from the experimental parameters n_∞ and $t_{0.8}$ as follows:

$$V^* = 4[(1 - 0.8)^2/t_{0.8}]n_\infty = 0.16n_\infty/t_{0.8} \qquad (3)$$

For any α value, the reaction rate V is

$$V = dn_t/dt = 25V^*(1 - \alpha)^2 \qquad (4)$$

Diffusion processes of the gaseous reagent into the pores do not affect noticeably the reaction kinetics since the same rate law is obeyed for gels with pore radii in the range of 23 to 400 Å (see Table 1).

It is highly probable that the reaction rate is related to the surface hydroxylic content. In silica gels this content involves, of course, both hydration water and silanol groups. It seems useless to make a distinction between the surface components since the kinetic laws, expressed in reduced coordinates, depend neither on the pretreatment temperature nor on the nature of the gel.

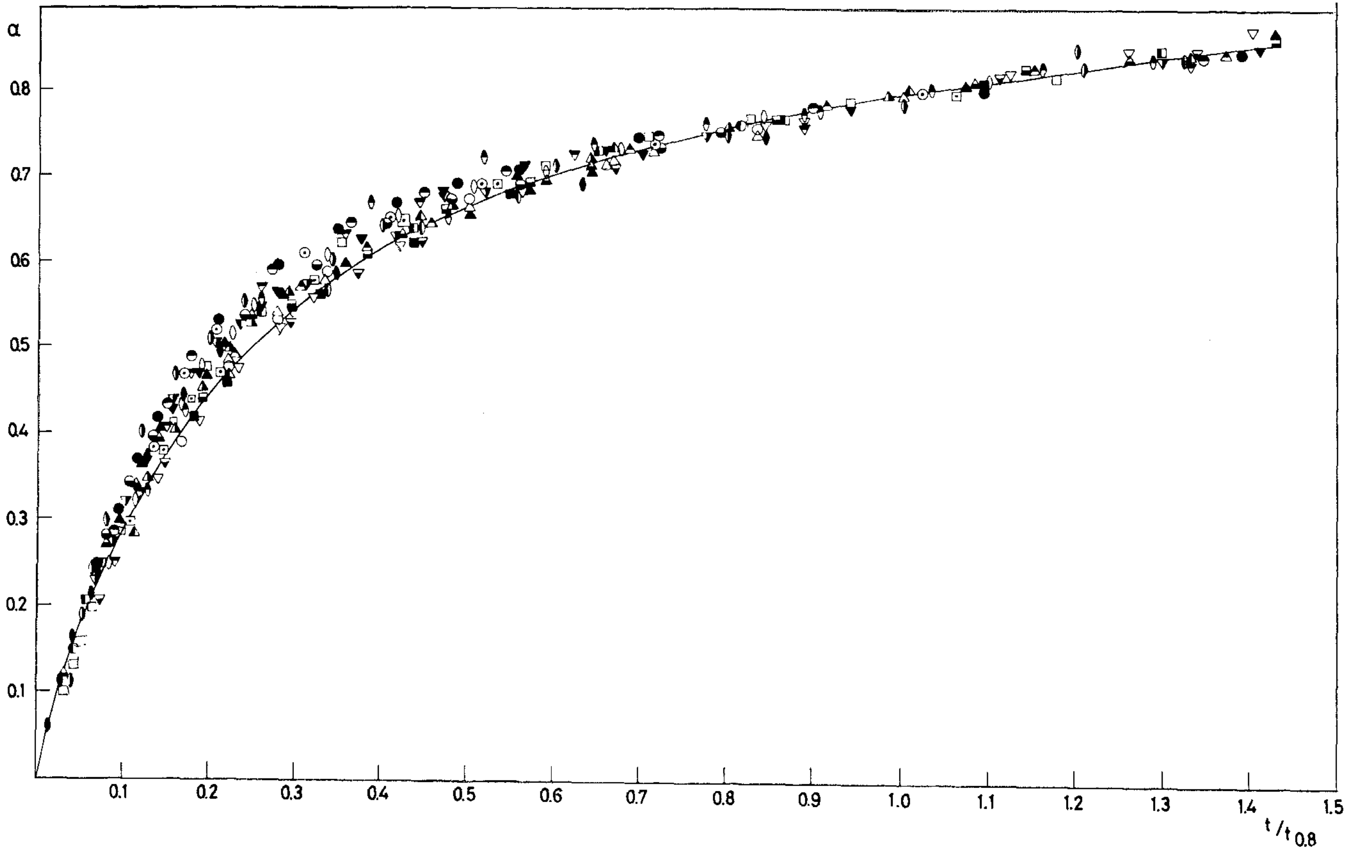


FIG. 6. Reaction of B_2H_6 with Aerogel I, expressed in reduced coordinates α and τ, under various experimental conditions: pretreatment temperature between 66°C and 640°C, gas pressure between 50 and 90 mm Hg, and reaction temperature between 0°C and 40°C. Solid line $\alpha = \tau/\tau + 0.25$.

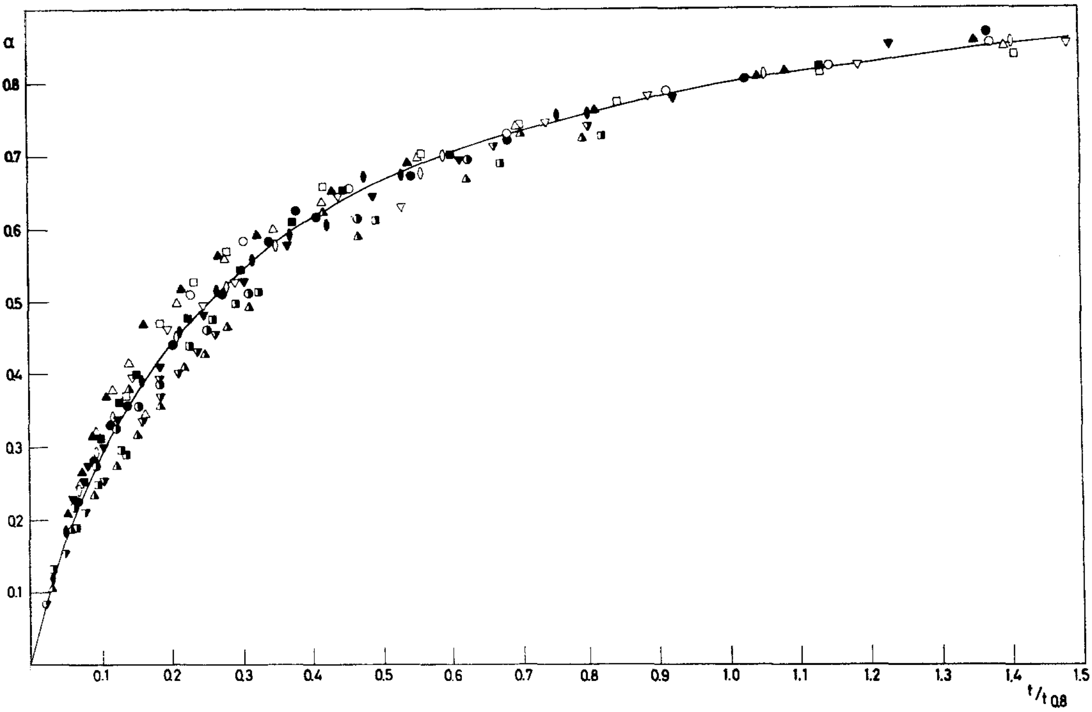


FIG. 7. Reaction of B_2H_6 with Aerogel II and Xerogel, expressed in reduced coordinates α and τ. B_2H_6 pressure, 50 mm Hg; Reaction temperature, 20°C; pretreatment temperature between 58°C and 515°C. Solid line: $\alpha = \tau/\tau + 0.25$.

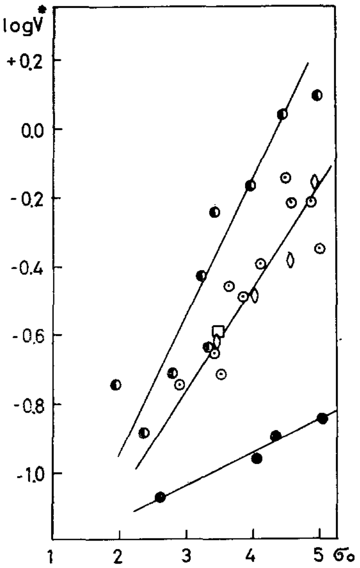


FIG. 8. $\log_{10} V^*$ (10^{-6} mole min^{-1}) against mobile hydrogen surface density σ_0 (H atom/100 Å^2) as determined with the organometallic reagents (*10*). B_2H_6 pressure, 50 mm Hg; reaction temperature: 0°C (●); 20°C (○); 40°C (◐). B_2H_6 pressure, 70 mm; reaction temperature 20°C, (☐). B_2H_6 pressure, 90 mm Hg: reaction temperature, 20°C (◇).

In order to correlate the reaction parameters to the surface hydroxylic contents, the initial mobile hydrogen surface density σ_0 (atoms per 100 Å^2), obtained from the reaction with $MgICH_3$ (*11, 13*) has been used. Figure 8 shows that linear relationships converging towards the same abscissa value, $\sigma_0 = 1.4$ H atoms/100 Å^2, are obtained by plotting log V^* versus σ_0. As expected from the apparent zero order with respect to the gaseous reagents, the slopes do not depend on the B_2H_6 pressures but they do, of course, change with the reaction temperature. The activation energy, calculated by plotting log V^* against T^{-1} for different σ_0 levels, increases linearly with σ_0, as shown in Fig. 9B.

From the numerical parameters obtained graphically from Figs. 8 and 9B, it is found

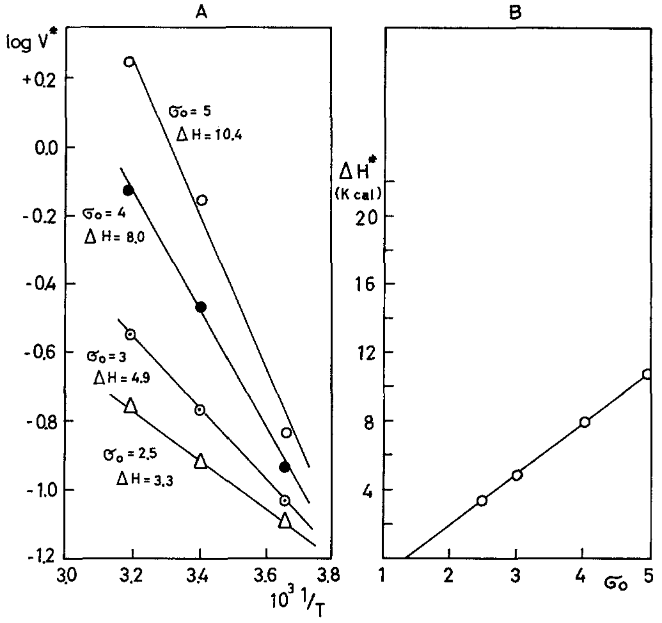


FIG. 9. A, $\log_{10} V^*$ against T^{-1} at different σ_0 levels; B, Activation energy ΔH^* (kcal mole^{-1}) against σ_0.

that

$$V = 1.57 \exp(\Delta S^*/R) \exp(-\Delta H^*/RT) (1-\alpha)^2\, 10^{-6} \text{ mole min}^{-1} \quad (5)$$

in which ΔS^* and ΔH^* are the activation entropy and enthalpy and that

$$\Delta S^* = 17.15[(\sigma_0/1.4) - 1] \text{ cal deg}^{-1}$$

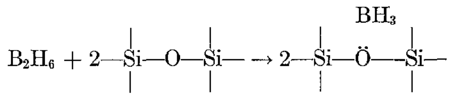
$$\Delta H^* = 4.28[(\sigma_0/1.4) - 1] \text{ kcal mole}^{-1}$$

Since (1-α) is directly proportional to the actual hydroxylic content, the reaction is apparently of the second order with respect to this variable parameter. The convergence point of the straight lines in Fig. 8 results from the fact that for an initial mobile hydrogen content of 1.4 atoms/100 Å^2, the activation energy reaches zero.

In samples outgassed in a temperature range high enough for lowering σ_0 below 1.4 (> 600°C), the H_2 evolution becomes extremely slow and the experimental results obtained under such conditions no longer correlate with those discussed above.

DISCUSSION

This discussion will aim to present a coherent reaction scheme for explaining the interaction of diborane with hydroxylic surfaces. The induction period has to be considered first since, obviously, it represents a very important feature of the reaction. Let us suppose that the induction time has the following meaning. Diborane molecules in contact with the adsorbent split into BH_3 groups which are adsorbed on surface Lewis basic sites. In silica gels, oxygen atoms of siloxane bridges may constitute such sites.



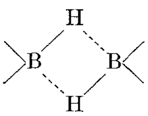
$$B_2H_6 + 2{-}\overset{|}{\underset{|}{Si}}{-}O{-}\overset{|}{\underset{|}{Si}}{-} \rightarrow 2{-}\overset{|}{\underset{|}{Si}}{-}\overset{BH_3}{\ddot{O}}{-}\overset{|}{\underset{|}{Si}}{-}$$

The time required for covering the active sites with a given concentration in BH_3 should be the induction time. The reaction of BH_3 groups with neighboring OH or H_2O should start when the stationary BH_3 concentration has reached an adequate value. This hypothesis is supported by several experimental arguments:

(1) Outgassing the samples markedly generates a larger number of siloxane bridges and consequently increases the surface concentration of BH_3 groups, provoking to some extent their recombination.

The induction period should then be longer, as is shown in Table 5. The lengthening of the induction period at higher pressure may be interpreted as an additional indication for such a process since BH_3 groups in the gas phase recombine with adsorbed BH_3.

(2) Baverez and Bastick (29), from desorption rate measurements, propose the same dissociation mechanism of B_2H_6 in BH_3 which are chemisorbed on surface oxygen atoms but they accept also that B_2H_6 molecules are adsorbed as well. Since the infrared bands relative to the bridged structure never appear in our spectra (cf. Table 4), it is believed that adsorption of B_2H_6 is of a physical nature only. From this viewpoint, the similarity of the results obtained for Aerogel and Xerogel is rather conclusive since it should be quite unlikely that B_2H_6 molecules chemisorbed on adsorbents with average pore radii as different as 23 and 400 Å (cf. Table 1) should be equally removed by outgassing between 30° and 50°C.

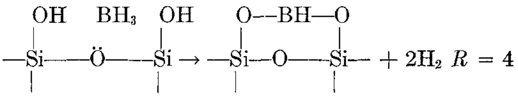


(3) That siloxane oxygen atoms are the adsorption sites fits the observation that the induction period is longer for samples outgassed at room temperature. Hydration water molecules would partially protect the surface by covering some active adsorption sites. Baverez and Bastick (*29*) also consider the oxygen atom of a siloxane bridge as the most probable adsorption site, as indicated by frequency shifts attributed to an electron transfer O: → B.

In order to explain the processes following the induction period, i.e., the reaction of chemisorbed BH_3 with hydration water molecules and silanols, the surface geometry, the hydrolysis ratios, and the infrared spectral features of surface radicals must be taken into account.

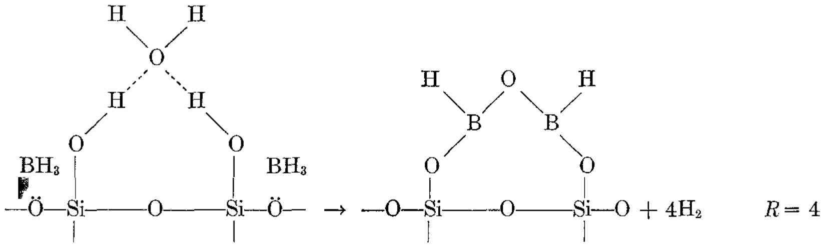
So far as the surface geometry is concerned, it is generally assumed (*11, 16*) that (a) a silicon atom does not bear two hydroxyls, otherwise the maximum hydroxyl surface density of 4.6 groups/100 Å^2 observed for a large variety of gels (*13*) should be too low; (b) the silica gel surface may be approximated to a cristobalite-like structure (*27*), as shown in Fig. 10; and (c) at relatively high hydration level a water molecule is linked through two hydrogen bonds with two surface hydroxyls while at low hydration level, H_2O is linked with one hydroxyl.

Point (a) rules out the reaction of B_2H_6 with a pair of hydroxyls brought by the same silicon. Because of unrealistic bond lengths due to the distribution of silicon tetrahedra [point (*b*)], the following reaction proposed by Baverez and Bastick (*29*) would be unacceptable on plane surfaces:



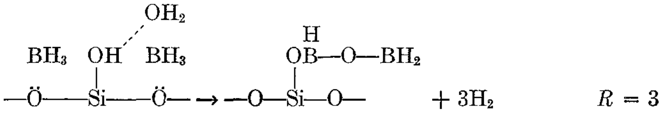
$$\underset{|}{\overset{OH}{-Si}}-\overset{BH_3}{\ddot{O}}-\underset{|}{\overset{OH}{Si}} \rightarrow -\underset{|}{Si}-O-\underset{|}{Si}- \overset{\text{(O--BH—O)}}{} + 2H_2 \quad R = 4$$

Distribution of hydroxyls and water molecules makes possible these reactions



(I)

and



(II)

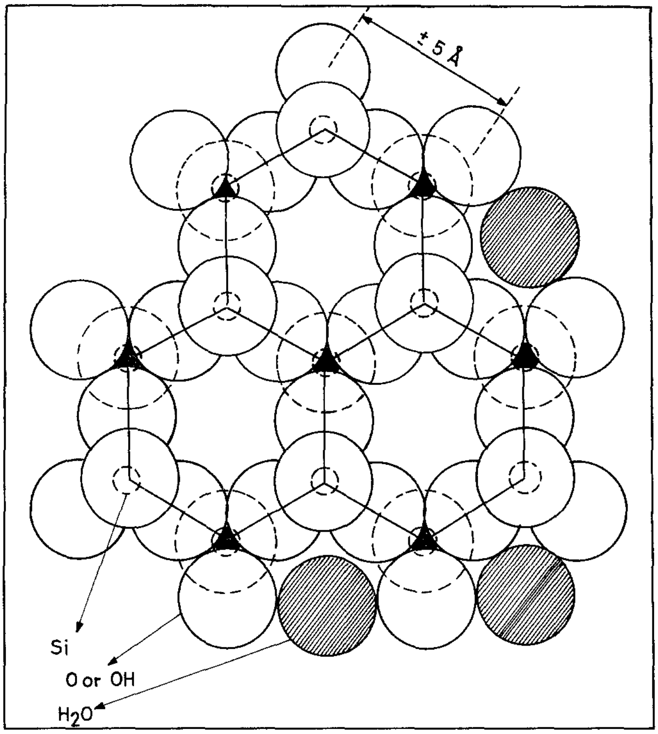
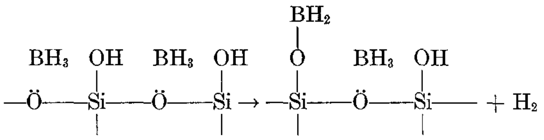


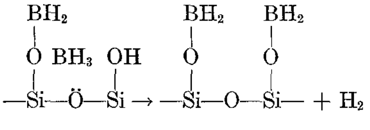
FIG. 10. Cristobalite structure projected on the *ab* plane.

The reaction with silanols would be



$$-\overset{\mathrm{BH_3}}{\ddot{\mathrm{O}}}-\overset{\overset{\mathrm{OH}}{|}}{\underset{|}{\mathrm{Si}}}-\overset{\mathrm{BH_3}}{\ddot{\mathrm{O}}}-\overset{\overset{\mathrm{OH}}{|}}{\underset{|}{\mathrm{Si}}}\rightarrow-\overset{\overset{\overset{\mathrm{BH_2}}{|}}{\overset{\mathrm{O}}{|}}}{\underset{|}{\mathrm{Si}}}-\overset{\mathrm{BH_3}}{\ddot{\mathrm{O}}}-\overset{\overset{\mathrm{OH}}{|}}{\underset{|}{\mathrm{Si}}}-+\mathrm{H_2}\qquad R = 1\qquad \mathrm{(III)}$$

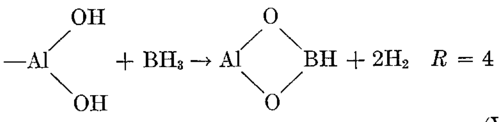
followed eventually by



$$-\overset{\overset{\overset{\mathrm{BH_2}}{|}}{\overset{\mathrm{O}}{|}}}{\mathrm{Si}}-\overset{\mathrm{BH_3}}{\ddot{\mathrm{O}}}-\overset{\overset{\mathrm{OH}}{|}}{\mathrm{Si}}\rightarrow-\overset{\overset{\overset{\mathrm{BH_2}}{|}}{\overset{\mathrm{O}}{|}}}{\mathrm{Si}}-\mathrm{O}-\overset{\overset{\overset{\mathrm{BH_2}}{|}}{\overset{\mathrm{O}}{|}}}{\mathrm{Si}}-+\mathrm{H_2}\quad R = 2\quad \mathrm{(IV)}$$

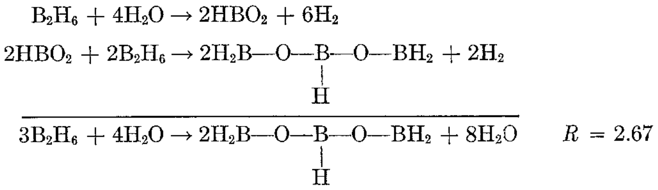
The latter occurs, of course, when the distances between adsorption sites and neighboring silanols are not too large. The primary hydrolysis ratio for the reaction of diborane with hydroxyls should then be found between 2 and 1 according to the surface hydroxyl content. This is in agreement with the experimental data (Table 3). The two schemes proposed for the reaction with hydrated surfaces are compatible with the spectroscopic features which rule out the formation of B_2H_5 radicals and BOH bonds, but show the existence of BH_2 or BH radicals (Table 4). These two schemes are also in agreement with hydrolysis ratios higher than 2. The reaction of diborane molecules with hydration water as proposed by Naccache and Imelik is not in contradiction with our infrared data but is not consistent with the significance of the induction period proposed in this work nor with hydrolysis ratios higher than 2 (Table 3). On hydrated surfaces, reactions typified by (I) and (II) would occur at the same time while in thoroughly dehydrated samples, reactions (III) and (IV) are most likely.

The situation for silicoalumina differs from the one pictured for silica gels mainly by virtue of the higher probability for an aluminum atom to bear two hydroxyls (*12*, *28*) and a higher surface hydration degree at low outgassing temperature (*12*). Therefore the following reaction is possible:



$$\text{—Al(OH)}_2 + BH_3 \rightarrow \text{Al(O)}_2\text{BH} + 2H_2 \quad R = 4 \qquad \text{(V)}$$

in agreement with the hydrolysis ratio of 3.85 found for gibbsite. The higher hydration degree at low temperature might explain the transient formation of metaboric acid observed by infrared spectroscopy (Table 4) as follows:



$$\begin{array}{l} B_2H_6 + 4H_2O \rightarrow 2HBO_2 + 6H_2 \\ 2HBO_2 + 2B_2H_6 \rightarrow 2H_2B\text{—O—}\underset{\displaystyle H}{\underset{|}{B}}\text{—O—}BH_2 + 2H_2 \\ \hline 3B_2H_6 + 4H_2O \rightarrow 2H_2B\text{—O—}\underset{\displaystyle H}{\underset{|}{B}}\text{—O—}BH_2 + 8H_2O \quad R = 2.67 \end{array} \qquad \text{(VI)}$$

although finely ground metaboric acid crystals do not react appreciably with B_2H_6.

For both silica gels and silicoalumina the secondary hydrolysis process, the introduction of water vapor into the reaction cell, leads to the decomposition of BH or BH_2 radicals and to the formation of BOH bonds as shown by the shift of the B–O stretching band from 1375 cm^{-1} to 1430 cm^{-1}.

In summary, the most probable mechanisms concerning the primary hydrolysis reaction are as follows:

	Silica gels	Silicoalumina
Hydrated sample	(I)–(IV)	(I)–(VI)
Dehydrated sample	(III), (IV)	(III), (IV), (V)
Appreciably dehydroxylated sample	(III)	(III)

The elimination of mechanism (V) for the appreciably dehydroxylated silicoalumina is justified by the findings by Basila (*30*) that residual OH groups left in these structures are silanol groups.

The interactions of these different reaction paths preclude the separate determinations of hydroxyls and surface water by the diborane procedure as well as the distinction between OH attached to aluminum, and those attached to silicon in silicoalumina.

As shown in Figs. 6 and 7, plotting the advancement of the hydrogen evolution (α) versus the reduced time (τ) fits a single function irrespective of the pretreatment temperature, i.e., irrespective of the water or hydroxyl surface densities. This suggests the operation of a single kinetic process which is not limited by a diffusion rate, since changing the gel texture as well as the reaction temperature does not deform noticeably the function α (τ), (Delmon, *31*).

As each of the reaction paths (I)–(IV) for silica gels, depends on the occurrence of a convenient BH_3 surface density, it is probable that the rate-limiting step is the continuous B_2H_6 dissociation required to maintain adequate BH_3 concentration on adsorption sites adjacent to hydroxyls and water molecules. The kinetics process may then be depicted as follows: Consider the schematic surface structure shown in Fig. 10. As the average silanol surface density approximates 4.6 OH/100 Å^2, the apparent area occupied by each hydroxyl group is of the order of magnitude of 22 Å^2. As the true O or OH packing is about 7 Å^2, two surface atoms out of three are, on the average, oxygen atoms. Thus each hydroxyl is theoretically surrounded by two potential adsorption sites. This is a maximum and for steric reasons due to the presence of hydration water molecules and to the surface geometry, the ratio hydroxyls/adsorption sites is probably nearer to 1.

This picture probably corresponds well to the actual situation for gels outgassed at low temperature; at higher temperature, the number of potential adsorption sites gains in importance since the hydration water molecules and further, the surface hydroxyls, are progressively removed. During the induction period the surface concentration reaches a critical value at which hydrogen evolution starts and the initial reaction rate, which according to relation (4) is equal to 25 V^*, is of course a function of the initial mobile hydrogen surface density σ_0. This is clearly shown in Fig. 8 by the linear relationship between log V^* and σ_0. The consumption of the surface BH_3 radicals, through mechanism (I)–(IV), requires the continuous dissociation of new B_2H_6 molecules. This step should be the rate-limiting process.

On surfaces pretreated at higher temperature, the number of adsorption sites is multiplied and the probability of the recombination $2BH_3 \rightarrow B_2H_6$ increases accordingly. This recombination process brings an explanation for this rather mysterious limit, $\sigma_0 = 1.4$ mobile hydrogen per 100 Å^2, which represents the convergence points of the linear functions log V^* (σ_0) shown in Fig. 8. The σ_0 would not be understood as a *lowest* limiting hydroxyl surface density, which is meaningless, but should correspond to a *highest* limiting density in adsorption sites. Above this limit the BH_3 recombination process becomes too fast to ensure the further reaction with residual OH. Using the same representation as above, 1.4 OH/100 Å^2 means that, on an average, more than four adsorption sites occupy adjacent positions on the surface.

This interpretation of the experimental results also makes much clearer the linear relationship observed between the activation energy ΔH^* and σ_0 as shown in Fig. 9B. Since the number of adsorption sites increases when σ_0 decreases through the dehydroxylation reaction $2\ OH \rightarrow\ > O + H_2O$ at higher outgassing temperature, the linear relationship with a *positive* slope between ΔH^* and σ_0 must be transformed into a linear relationship with a *negative* slope between ΔH^* and the number of adsorption sites. The activation energy is thus higher when the probability of a B_2H_6 meeting adjacent sites is lower, which seems obvious if the rate-limiting process is the splitting of diborane molecules.

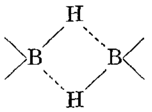
It remains to explain the apparent second order of the rate process with respect to the time-variable surface hydroxyl contents, as evidenced by relationship (5). Regardless of the reaction path, each time a hydrogen molecule is produced, a surface hydrogen atom is consumed, but a number of BH_3 radicals varying between 2 and 1 is used according to the reaction schemes (I)–(IV). The maintenance of a BH_3 surface concentration adequate to ensure the evolution of hydrogen requires the dissociation rate process $B_2H_6 \rightarrow 2BH_3$ to be variable with time, since the number of surface hydrogen atoms and the hydrolysis ratio decreases continuously. On the other hand the rate of the recombination process $2BH_3 \rightarrow BH_6$ is determined mainly by the pretreatment conditions and does not change, in the first instance, in the course of the reaction.

Therefore, to arrive to an explanation of the reaction order, the reaction rate must necessarily be expressed in terms of BH_3 surface concentration instead of hydrogen molecules evolved. This should require a more sophisticated treatment than is attempted here.

CONCLUSIONS

Diborane molecules do not react as such with hydroxylic surfaces; B_2H_6 is dissociated and BH_3 groups are probably adsorbed on oxygen atoms acting as Lewis basic sites. For this reason the reaction is actually preceded by an induction period.

The reaction of BH_3 with hydration water is characterized by hydrolysis ratios >2 while the reaction with silanols occurs with hydrolysis ratios in the range of values $\leqslant 2$. BH_2 and BH radicals linked to oxygen atoms are formed by the reaction with surface water as well as with hydroxyls. Neither bridged



structures nor BOH bonds were observed in silica gels treated by diborane; however for a highly hydrated silicoalumina, metaboric acid might be an intermediate reaction product.

The distinction between hydration water molecules and surface hydroxyls seems impossible on the basis of the various reaction schemes necessary to explain the hydrolysis ratios and the infrared spectral features. The rate process is apparently of the second order with respect to the surface hydroxyl content and a single kinetic mechanism is operating regardless of the pretreatment conditions, so long as the surface density (including water + OH) is higher than 1.4 mobile H atoms per 100 Å^2. This is interpreted by assuming that the rate-limiting process is the dissociation of B_2H_6 into BH_3 groups adsorbed on surface oxygen atoms. Diffusion operating mechanisms do not play a determining role, as shown by the similarity of the kinetic data obtained for gels with very different textures.

ACKNOWLEDGMENTS

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