

**Table I.**  $G_H (= G_{HD} + 2G_{H_2})$  for Reaction 1<sup>a</sup>

Sample	Surface area, m. <sup>2</sup> /g.	$G_H$ , molecules/100 e.v.			
		Fraction of molecules on surface	Total energy absorbed	Surface only	Ratio
$\alpha$ -Cristobalite	10.2	$1/128$	0.60	75	14.7
Vitreous silica	4.9	$1/260$	0.20	52	10.2
Quartz	4.0	$1/385$	0.06 <sup>b</sup>	20 <sup>b</sup>	3.9
Low area gel	80	$1/50$	0.60	30	5.9
Medium area gel	330	$1/4.2$	2.3	9.7	1.9
High area gel	550	$1/2.2$	2.3	5.1	1.0
Pure gel	425	$1/3.1$	2.3	7.1	1.4
SiCl <sub>4</sub> prepn.					
Ultrapure gel	560	$1/2.2$	2.3	9.7	1.9
SiCl <sub>4</sub> prepn.					
0.01 Al-SiCl <sub>4</sub> prepn.	450	$1/3.0$	3.2	9.6	1.9

<sup>a</sup> Samples degassed at 410° and annealed at 350° between irradiations;  $G$  values for lowest dose rates. <sup>b</sup> Maximum.

deposited in or near the surface results in chemical reaction. The fraction of the silica molecules on the silica surface can be calculated using only the density, surface area, molecular weight, and the formulas of elementary geometry. These fractions are gathered in the third column of Table I. Yields based on the energy absorbed only by these silica surface molecules can then be calculated by multiplying column 4 by the inverse of column 3, and are listed in column 5. Most of these "surface only" yields appear much too large; a more reasonable yield would lie in the range 3 to 6 molecules/100 e.v. Using 5.1 (the lowest "surface only" figure) as a reasonable estimate of the true yield, one can calculate a ratio by which the "surface only" yield is too great.

This ratio can be interpreted in several ways. If we assume that subsurface excitation events appear on the surface and result in the reaction of one or two molecules, the ratio gives the average number of subsurface layers participating in the reaction and hence the migration distance<sup>6</sup> or the size of a collective excitation<sup>7</sup> in molecular diameters. It does not seem reasonable that the size of a collective ionization should vary with particle size; indeed, one would expect that, as the particle size drops below that of a collective ionization, the yield would decrease, and this is not observed. Color centers do not afford a satisfactory explanation either since their yield is too low, and only those on the surface react<sup>8</sup> (low-area silicas are blue after this reaction). On the other hand, if we assume that only excitations occurring directly on the surface are important, the ratio must be looked upon as the average length of a surface chain.<sup>9</sup> Hence the most reasonable explanation for the ratio of column 6 of the table is that this number is the mean migration distance in molecular diameters or the average length of a surface chain. It is logically consistent that the energy mi-

(6) This terminology is based on the model in ref. 2. Similar treatment of the data for MgO in ref. 2 gives an average migration distance of 10 molecular diameters.

(7) This is the terminology of J. L. Magee, *Ann. Rev. Phys. Chem.*, **12**, 389 (1959).

(8) H. W. Kohn, *J. Chem. Educ.*, in press.

(9) H. W. Kohn, *J. Phys. Chem.*, **68**, 3129 (1964).

gration distance does not exceed the particle size, or alternatively that the surface chain length does not exceed the number of surface molecules; *i.e.*, interparticle migration of intermediates is not required to explain the data.

The nature of the defects which compete with the surface for radiation energy is not explained by the data in the table. If regions of disorder or lattice defects dissipate energy, one would expect vitreous silica to be inferior as an energy-transfer agent to both  $\alpha$ -cristobalite and quartz. It obviously is not. Impurities do not have an overriding effect on the yield either, especially on the "surface only" value.

We also note that the yields for reaction 1 are lower than those for the corresponding reaction



indicating that the yield-determining steps are initiated on the gel surface, and that diffusion is probably not yield determining.<sup>10</sup> Both the isotope effect and the dose rate effect indicate that a reactant path and a deactivation process compete for reactive intermediates with reactions of different order.

Alumina and silica-alumina also show radiation-induced exchange decomposition like silica but the data at present are too fragmentary to include in this communication.

(10) N. H. Sagert (private communication) has observed a similar isotope effect in the system cyclohexane-silica gel; see also ref. 3a.

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## Preparation and Properties of *i*-B<sub>9</sub>H<sub>15</sub><sup>1</sup>

Sir:

We wish to report that a new, unstable boron hydride is formed by treatment of KB<sub>9</sub>H<sub>14</sub> with HCl at -80°. This hydride is thermally unstable and relatively indirect methods have been used to characterize it.

In a typical preparation, 0.150 g. of KB<sub>9</sub>H<sub>14</sub> was treated with a measured excess of liquid hydrogen chloride at -78° for 30 min. in a sealed tube. No hydrogen was evolved during this time. Unreacted hydrogen chloride was distilled from the flask and final traces were removed by prolonged pumping at -50°. One mole of hydrogen chloride was retained by the reaction mixture per mole of salt used. The solid product was extracted with dry pentane and filtered using a chilled filtration apparatus. Decomposition with loss of hydrogen occurred at -30° or above, but analysis of the extract showed that no chloride was retained in the filtrate. A separately prepared sample was similarly extracted and treated with an excess of methanol for 9 hr. at 100°. The hydrogen formed in this reaction was measured volumetrically as a gas and the boron determined by titrating boric acid as the D-mannitol complex using the identical pH method. The observed ratio of hydrogen of alcoholysis to boron was 2.30, in good agreement with the theoretical 2.33 pre-

(1) Studies of Boranes. XIX. For paper XVIII of this series see D. MacLean, P. Keller, and R. Schaeffer, *Chem. Commun.*, in press.

dicted for methanolysis of a  $B_9H_{15}$  hydride. Direct determination of the molecular weight of the new hydride proved impossible owing to its low thermal stability. To demonstrate that the hydride retained the nine boron unit of the initial salt, a toluene solution of the hydride was allowed to decompose in the presence of a large excess of acetonitrile, and a quantitative yield of  $B_9H_{13} \cdot CH_3CN$  was recovered from the reaction mixture. The product was identified by comparison of its X-ray powder pattern with that calculated for the compound from the single crystal data of Wang, *et al.*<sup>2</sup>

The  $^{11}B$  n.m.r. spectrum was recorded using a Varian DP60 nuclear magnetic resonance spectrometer operating at 19.3 Mc./sec. Throughout the determination of the spectrum the sample was maintained between  $-40$  and  $-60^\circ$  using standard Varian accessories. The spectrum was substantially simpler than that of the previously isolated  $B_9H_{15}$ .<sup>3</sup> The spectrum consisted of a very broad low-field doublet ( $\delta = 5$  p.p.m.,  $J = 136$  c.p.s.) and two overlapping high-field doublets ( $\delta = 31$  p.p.m.,  $J = 163$  c.p.s.;  $\delta = 44$  p.p.m.,  $J = 163$  c.p.s.). The integrated ratio of the high-field doublets to the low-field doublet was only 1.9, compared to the expected value of 2.0, but was somewhat uncertain owing to the extreme broadness of the downfield doublet. This spectrum strongly suggests a structure with approximate  $C_{3v}$  symmetry derived by removal of a triangle of borons from an icosahedron.

Only for the case of  $B_{10}H_{12}$  has isomerism previously been observed in the binary boron hydride series. No sound theoretical reasons exist for the lack of a more general series of isomers, although considerable differences in stability may be expected. It is interesting to note that the rearrangement from the unstable isoform to the more stable normal form does not occur to a measurable extent. If the above structure is correct, migration of a boron atom would be required.

It should be noted that under very different conditions reaction of a  $B_9H_{14}^-$  salt with polyphosphoric acid has been shown to form hexaborane(10).<sup>4</sup>

(2) F. E. Wang, P. G. Simpson, and W. N. Lipscomb, Jr., *J. Chem. Phys.*, **35**, 1335 (1961).

(3) A. B. Burg and R. Kratzer, *Inorg. Chem.*, **1**, 725 (1962).

(4) H. A. Beall and W. N. Lipscomb, *ibid.*, **3**, 1783 (1964).

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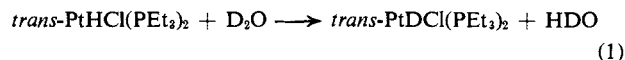
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### Isotopic Exchange of a Hydridoplatinum(II) Complex with Deuterium Oxide

Sir:

We wish to describe a kinetic study of a novel substitution reaction of a square-planar complex, involving the isotopic exchange



$\text{trans-PtHCl}(\text{PEt}_3)_2$  was prepared by the method of Chatt and Shaw<sup>1</sup> and its isotopic exchange with  $\text{D}_2\text{O}$

(1) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 5075 (1962).

examined in  $\text{D}_2\text{O}$ -acetone solutions. The kinetic measurements were made by removing samples of the reaction mixture periodically, adding them to benzene containing an excess of ammonia to quench the reaction, freeze-drying the resulting mixture, and extracting the residual solid with benzene to dissolve the  $\text{PtHCl}(\text{PEt}_3)_2$  and  $\text{PtDCl}(\text{PEt}_3)_2$ . The infrared spectrum of the benzene solution was recorded and the extent of isotopic exchange determined from the decrease in the absorbance of the Pt-H stretching band at  $2196 \text{ cm}^{-1}$ , relative to the constant absorbance at  $2876 \text{ cm}^{-1}$  corresponding to one of the C-H stretching frequencies of the triethylphosphine which was unaffected by the exchange reaction. Using this procedure the kinetics of the exchange reaction were determined at  $30^\circ$  in  $\text{D}_2\text{O}$ -acetone solutions containing 25 and 10 vol. %  $\text{D}_2\text{O}$ . Among the kinetic variables examined were the effects of the concentrations of  $\text{D}^+$  and  $\text{Cl}^-$ , each of which was varied from 0 to  $6.4 \times 10^{-3} M$  (using  $\text{ClO}_4^-$  and  $\text{Li}^+$ , respectively, to hold the ionic strength constant at  $6.4 \times 10^{-3} M$ ).

Isotopic exchange, according to reaction 1, was found to be very slow (corresponding to a first-order rate constant of less than  $10^{-5} \text{ sec}^{-1}$ ) in the absence of added acid, but was accelerated by  $\text{DClO}_4$  and, even more markedly, by  $\text{DCl}$ . The acceleration by  $\text{DCl}$  is in accord with the earlier qualitative observation of Chatt and Shaw.<sup>1</sup>

The rate law for the exchange reaction in 25%  $\text{D}_2\text{O}$ -75% acetone was found to be

$$-d[\text{PtHCl}(\text{PEt}_3)_2]/dt = (k_1 + k_2[\text{Cl}^-])[D^+][\text{PtHCl}(\text{PEt}_3)_2] \quad (2)$$

where  $k_1 = 4.1 \times 10^{-2} M^{-1} \text{ sec}^{-1}$  and  $k_2 = 6.0 M^{-2} \text{ sec}^{-1}$ .

The rates of both the  $\text{Cl}^-$ -independent and  $\text{Cl}^-$ -dependent paths exhibited an inverse dependence on the  $\text{D}_2\text{O}$  content of the solvent mixture, the effect being much greater for the latter path. On reducing the  $\text{D}_2\text{O}$  content to 10 vol. %, the rates of both paths remained first order in  $\text{D}^+$ , whereas the apparent kinetic dependence of the  $\text{Cl}^-$ -dependent path on the  $\text{Cl}^-$  concentration became higher than first order. The empirical rate law under these conditions was found to be

$$-d[\text{PtHCl}(\text{PEt}_3)_2]/dt = (k_1 + k_2'[\text{Cl}^-]^{1.4})[D^+][\text{PtHCl}(\text{PEt}_3)_2] \quad (3)$$

where  $k_1 = 7.3 \times 10^{-2} M^{-1} \text{ sec}^{-1}$  and  $k_2' = 36 M^{-2.4} \text{ sec}^{-1}$ .

The acid catalysis of the exchange of  $\text{trans-PtHCl}(\text{PEt}_3)_2$  with  $\text{D}_2\text{O}$  is somewhat unexpected in view of the generally accepted assignment of anionic character to the exchanging hydride ligand.<sup>2</sup> The most likely site of protonation of the complex is considered to be the platinum atom and, in line with this, the following mechanism involving reversible oxidation of the platinum(II) is proposed for the exchange path which is first order in both  $\text{D}^+$  and  $\text{Cl}^-$ . The  $\text{Cl}^-$ -independent path may be accounted for by an analogous mechanism involving a solvent molecule in place of the  $\text{Cl}^-$  ion.

The postulated intermediate of the mechanism depicted by eq. 4, which may have either a *cis* or *trans* configuration, was not detected under our conditions.

(2) J. Chatt, *Proc. Chem. Soc.*, 318 (1962).