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Note

# Kinetics of ortho-carborane formation revisited

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## Abstract

A kinetic study of ortho-carborane formation focusing on the reaction of various decaborane adducts  $[B_{10}H_{12}L_2; L=Me_2S, Ph_2S, tert-Bu_2S, (C_6F_5)_2S, MeSPh, MeSC_6F_5, MeS(sec-Bu)]$  with three acetylenes (propargyl bromide, 2-butyne-1,4-diacetate, 1-nonyne) has been carried out. For a given acetylene, the rate constants decrease with both an increase in the electronegativity and/or an increase in size of substituents on sulfur. Yields of orthocarborane have been shown to increase as the size and/or basicity of the Lewis base increases and, for a given adduct, with the lower basicity of the acetylene.

Keywords: Ortho-carborane; Kinetics

## 1. Introduction

Since the icosahedral carboranes were first reported in 1963, a wide variety of the so-called ortho-carboranes have been prepared and studied and still are the subject of research [1]. However, little attention has been given to the kinetics of ortho-carborane formation, the latest study being that of Hill et al. [2].

The most common method for the preparation of orthocarborane is through the use of diligand derivatives of decaborane and acetylenes as shown below.

$$B_{10}H_{14} + 2L \ (L = Lewis \ base) \rightarrow B_{10}H_{12}L_2 + H_2$$
 (1)

$$B_{10}H_{12}L_2 + RC \equiv CR' \rightarrow B_{10}H_{10}C_2RR' + 2L + H_2$$
(2)

A few kinetic studies [3–7] on the formation of  $B_{10}H_{12}L_2$ have indicated that the reaction of decaborane and the Lewis base follows second order kinetics, being first order with respect to each reactant. Although the mechanisms for the reactions have been proposed, no systematic study of the effect of different Lewis bases on the reactions has yet been reported [8–10].

We report here a systematic kinetic study of both the above reactions with a series of different Lewis bases in order to examine their steric and electronic contributions. We also present an efficient way to maximize the yield of orthocarborane.

## 2. Experimental

## 2.1. Reagents

All solvents were dried over sodium; all sulfides and acetylenes were distilled, and decaborane was sublimed at 60°C and  $1 \times 10^{-4}$  torr prior to use.

## 2.2. Kinetic procedure

A 0.5-0.8 M solution of decaborane in dry benzene or toluene was placed in a 100 ml three-necked flask fitted with a ground joint thermometer, a serum cap and connected through a condenser to a gas burette of 50 or 100 ml capacity, depending on the rate of gas evolution during an experiment. The solution was heated to the desired temperature in an oil bath and was stirred with a magnetic stirrer. After attaining the temperature, a measured amount (twice the number of moles of decaborane) of dialkyl or diaryl sulfide (L) was injected into the solution via a syringe. The rate of evolution of hydrogen gas was determined by measuring the volume of hydrogen evolved. Sufficient time was allowed for completion of the reaction by leaving the solution for at least 24 h, after collecting the gas volume data of B<sub>10</sub>H<sub>2</sub>L<sub>2</sub> formation. While the decaborane adduct  $(B_{10}H_2L_2)$  is still in solution, an equimolar amount of one of the acetylenes was injected into the solution via a syringe and, in a similar fashion, the rate of hydrogen gas evolution was recorded. Gas volumes were corrected for the saturated vapor pressure of the solvents.

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## 2.3. Extraction of carborane

After collecting all the hydrogen gas evolution data, the final mixture was allowed to heat to the reflux temperature of the solvent with continuous stirring for at least 48 h. The solution was allowed to cool to room temperature and was then evaporated to dryness under reduced pressure. The residue was dissolved in hot hexane and filtered hot to remove any hexane insoluble residue. *Ortho*-carborane was precipitated by refrigeration of the filtrate, and was dried under vacuum.

# 3. Results and discussion

#### 3.1. Reaction kinetics

The reactions of decaborane with various Lewis bases (L) were investigated over a temperature range of  $35-95^{\circ}$ C. Reactions were carried out by monitoring the rate of hydrogen gas evolution. The number of moles of gas evolved was related to the number of moles of decaborane reacted according to Eq. (1).

The data indicated that the gas evolution was first order with respect to both decaborane and Lewis base. The equation used for the calculation of the rate constant was

Rate =  $d[B_{10}H_{14}]/dt = dx/dt$ 

$$=k([D_{o}] - x)([L_{o}] - 2x) = 2k([D_{o}] - x)^{2}$$

Table 1

Activation parameters and kinetic data for decaborane Lewis base (L) adducts  $(B_{10}H_{12}L_2)$  formation

or, upon integration and rearrangement,

$$(1/[D_0] - x) - (1/[D_0]) = 2kt$$

where  $[D_o]$  and  $[L_o]$  are the initial concentrations of  $B_{10}H_{14}$ and L respectively, *x* is the concentration of  $B_{10}H_{12}L_2$  as well as  $H_2$  formed at time *t* of the reaction, and  $2[D_o] = [L_o]$  since stoichiometric amounts of decaborane and L were taken for all reactions. The graphically obtained rate constant values are given in Table 1. In all cases, the data were collected to 75% completion.

While the decaborane adduct,  $B_{10}H_{12}L_2$  was still in solution, a stoichiometric amount of the acetylene was added and kinetic data were recorded over a temperature range of 35–85°C. A plot of concentration with time indicated that the hydrogen gas evolution was first order in both  $B_{10}H_{12}L_2$  and acetylene. The rate constants listed in Table 2 were calculated in a similar way as that shown above for the formation of  $B_{10}H_{12}L_2$ .

## 3.2. Decaborane adduct formation

Nucleophilic alkylation of decaborane is known to involve the boron atoms of the borane at positions 6 and 9 [11]. The reactions of dialkyl or diaryl sulfides with decaborane probably involve attack by a basic sulfur atom at the most electropositive sites (positions 6 and 9) in decaborane; so the reactions should be favored by subsituents which increase the availability of electrons on the sulfur atom. The data

L <sup>a</sup>	<i>Т</i> (°С)	$k (s^{-1} M^{-1})$	$\Delta H^{\neq} (\pm 0.6)$ (kJ mol <sup>-1</sup> )	$\Delta S^{\neq} (\pm 1.0) (\text{J mol}^{-1} \text{ K}^{-1})$
Me <sub>2</sub> S	46.0	$1.40 \times 10^{-4}$	63.97	- 119.06
2.4	55.0	$2.76 \times 10^{-4}$		
	65.0	$5.73 \times 10^{-4}$		
Ph <sub>2</sub> S	46.1	$6.70 \times 10^{-6}$	77.72	-101.25
2	55.0	$1.55 \times 10^{-5}$		
	64.9	$3.67 \times 10^{-5}$		
MeSPh	46.0	$1.62 \times 10^{-5}$	66.60	-128.76
	55.1	$3.31 \times 10^{-5}$		
	64.9	$7.01 \times 10^{-5}$		
Bu <sup>t</sup> <sub>2</sub> S	55.0	$4.48 \times 10^{-6}$	108.18	-18.89
-	65.0	$1.43 \times 10^{-5}$		
	74.9	$4.62 \times 10^{-5}$		
MeSBu <sup>t</sup>	46.0	$1.45 \times 10^{-5}$	72.09	-112.45
	55.1	$3.16 \times 10^{-5}$		
	65.1	$7.05 \times 10^{-5}$		
$(C_{6}F_{5})_{2}S$	75.0	$2.25 \times 10^{-5}$	137.58	59.79
	84.9	$9.39 \times 10^{-5}$		
	95.1	$3.12 \times 10^{-4}$		
MeSC <sub>6</sub> F <sub>5</sub>	54.9	$1.72 \times 10^{-5}$	105.35	- 16.25
0.5	65.0	$5.49 \times 10^{-5}$		
	75.0	$1.67 \times 10^{-4}$		
MeSBu <sup>s</sup>	46.1	$2.67 \times 10^{-5}$	65.55	-127.88
	55.0	$5.41 \times 10^{-5}$		
	64.9	$1.13 \times 10^{-4}$		

<sup>a</sup>  $Bu^t = tert-butyl; Bu^s = sec-butyl.$ 

Table 2
Activation parameters and kinetic data for carborane formation from $B_{10}H_{12}L_2$ (L=Lewis base) and proparely bromide

L <sup>a</sup>	<i>T</i> (°C)	$k (s^{-1} M^{-1})$	$\frac{\Delta H^{\neq} \ (\pm 0.6)}{(\text{kJ mol}^{-1})}$	$\Delta S^{\neq} (\pm 1.0)$ (J mol <sup>-1</sup> K <sup>-1</sup> )	Yield (%)
Me <sub>2</sub> S	46.0	$5.52 \times 10^{-4}$	129.44	97.27	84.0
	55.1	$2.14 \times 10^{-3}$			
	65.0	$0.04 \times 10^{-3}$			
Ph <sub>2</sub> S	46.0	$4.99 \times 10^{-5}$	60.80	- 137.52	84.1
	54.8	$9.67 \times 10^{-5}$			
	65.1	$1.91 \times 10^{-4}$			
MeSPh	46.1	$7.17 \times 10^{-5}$	128.43	77.24	84.5
	55.0	$2.85 \times 10^{-4}$			
	65.0	$1.15 \times 10^{-3}$			
Bu <sup>t</sup> <sub>2</sub> S	46.1	$3.15 \times 10^{-5}$	43.12	- 196.71	89.0
-	55.1	$5.06 \times 10^{-5}$			
	65.2	$8.30 \times 10^{-5}$			
MeSBu <sup>t</sup>	54.0	$6.71 \times 10^{-5}$	70.13	- 105.83	87.3
	54.9	$1.44 \times 10^{-4}$			
	65.1	$3.14 \times 10^{-4}$			
$(C_6F_5)_2S$	46.2	$5.11 \times 10^{-5}$	58.76	- 143.69	87.5
	55.0	$9.81 \times 10^{-5}$			
	65.0	$1.87 \times 10^{-5}$			
MeSC <sub>6</sub> F <sub>5</sub>	54.8	$7.70 \times 10^{-5}$	93.21	-40.79	85.6
	65.1	$2.13 \times 10^{-4}$			
	75.0	$5.79 \times 10^{-4}$			
MeSBu <sup>s</sup>	46.0	$7.46 \times 10^{-5}$	127.38	74.24	83.8
	55.0	$2.89 \times 10^{-4}$			
	64.9	$1.17 \times 10^{-3}$			

<sup>a</sup>  $Bu^t = tert-butyl; Bu^s = sec-butyl.$ 

Table 3

Cone angles and electronic contributions for different substituents on the Lewis bases (L) in  $B_{10}H_{12}L_2$  adducts and AH for the formation of the adducts

L <sup>a</sup>	Cone angle $b^{(\circ)}$	Electronic contribution <sup>b</sup>	$\Delta H^{\neq}  (\mathrm{kJ}  \mathrm{mol}^{-1})$	
Me <sub>2</sub> S	180	5.2	63.97	
MeSPh	185	6.9	66.60	
Ph <sub>2</sub> S	210	8.6	77.72	
MeSBu <sup>t</sup>	216	_	72.09	
Bu <sup>t</sup> <sub>2</sub> S	252	_	108.18	
MeSC <sub>6</sub> F <sub>5</sub>	_	13.8	105.35	
$(C_6F_5)_2S$	-	22.4	137.58	

<sup>a</sup>  $Bu^t = tert-butyl.$ 

<sup>b</sup> Values obtained from Ref. [12].

(Table 1) indicate that dimethyl sulfide reacts faster than the other sulfides considered. The relative reaction rates at 55°C for the reaction of Me<sub>2</sub>S and decaborane when compared to other sulfides studied here are: MeS–sec-Bu, 5.1; MeSPh, 8.3; MeSBu<sup>t</sup>, 8.7; Ph<sub>2</sub>S, 17.8; Bu<sup>t</sup><sub>2</sub>S, 61.6. The enthalpies of activation,  $\Delta H^{\neq}$ , increase in the same order with the exception of MeSC<sub>6</sub>F<sub>5</sub>, where the electron withdrawing group, C<sub>6</sub>F<sub>5</sub>, lowers the basicity of the sulfide. For (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>S the activation enthalpy is much higher. In almost all the systems studied, with the exception of (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>S, the activation entropy,  $\Delta S^{\neq}$ , has a negative value.

Steric effects may also affect the reaction rate. The size of the  $R_2S$  groups may be quantified in terms of cone angle and the quantitative measurement of the electronic contributions

for the groups attached to the sulfur atom can be expressed in terms of the electronic factor as defined by Tolman [12]. Table 3 lists cone angles and electronic factors for some of the sulfides. Clearly the  $\Delta H^{\neq}$  values increase with increasing size and/or electronic factor.

Based on the present experimental and previous results (Ref. [2] and references cited therein), the reaction mechanism may involve the following two steps:

$$B_{10}H_{14} + L \rightarrow B_{10}H_{14}L$$

$$B_{10}H_{14}L + L \rightarrow B_{10}H_{12}L_2 + H_2$$

Table 4
Activation parameters and kinetic data for carborane formation from different acetylenes and $B_{10}H_{12}L_2$ (L = Lewis base)

$B_{10}H_{12}L_2 \ ^a$	Acetylene	<i>Т</i> (°С)	$k (s^{-1} M^{-1})$	$\Delta H^{\neq} (\pm 0.6)$ (kJ mol <sup>-1</sup> )	$\Delta S^{\neq} (\pm 1.0)$ (J mol <sup>-1</sup> K <sup>-1</sup> )	Yield (%)
$B_{10}H_{12}(Me_2S)_2$	Propargyl	46.0	$5.52 \times 10^{-4}$	129.44	97.27	84.0
	bromide	55.1	$2.14 \times 10^{-3}$			
		65.0	$9.0 \times 10^{-3}$			
	2-Butyne-1,4-	46.0	$3.12 \times 10^{-4}$	119.28	60.71	82.7
	diacetate	55.0	$1.08 \times 10^{-3}$			
		64.9	$4.12 \times 10^{-3}$			
	1-Nonyne	46.1	$1.54 \times 10^{-4}$	80.60	-66.10	31.6
	·	55.2	$3.76 \times 10^{-4}$			
		65.0	$8.97 \times 10^{-4}$			
$B_{10}H_{12}(Ph_2S)_2$	Propargyl	46.0	$4.99 \times 10^{-5}$	60.80	-137.52	84.1
	bromide	54.8	$9.67 \times 10^{-5}$			
		65.1	$1.91 \times 10^{-4}$			
	2-Butyne-1,4-	45.9	$4.01 \times 10^{-5}$	56.12	- 153.99	87.5
	diacetate	55.1	$7.42 \times 10^{-5}$			
		65.2	$1.39 \times 10^{-4}$			
	1-Nonyne	46.0	$2.87 \times 10^{-5}$	54.04	-163.29	33.8
		54.9	$5.17 \times 10^{-5}$			
		65.0	$9.52 \times 10^{-5}$			
$B_{10}H_{12}(Bu_{\ 2}^{t}S)_{\ 2}$	Propargyl	46.1	$3.15 \times 10^{-5}$	43.12	- 196.71	89.0
	bromide	55.1	$5.06 \times 10^{-5}$			
		62.5	$8.30 \times 10^{-5}$			
	2-Butyne-1,4-	46.0	$3.28 \times 10^{-5}$	40.64	-204.15	87.7
	diacetate	55.0	$5.11 \times 10^{-5}$			
		64.9	$8.19 \times 10^{-5}$			
	1-Nonyne	46.2	$2.69 \times 10^{-5}$	30.09	-238.10	38.1
		55.1	$4.07 \times 10^{-5}$			
		65.0	$5.89 \times 10^{-5}$			

<sup>a</sup>  $Bu^t = tert-butyl; Bu^s = sec-butyl.$ 

A negative  $\Delta S^{\neq}$  is expected for the slow step consistent with the observed data.

## 3.3. Ortho-carborane formation

Hill et al. [2] reported that acetylenes with functional groups attached directly to the C=C linkage gave very low yields of carborane (<10%) and therefore kinetic studies with those acetylenes would not be very meaningful. Therefore, we have chosen propargyl bromide to react with all of the decaborane adducts since the highest yields of orthocarboranes were obtained with this acetylene. Two other acetylenes, 2-butyne-1,4-diactetate and 1-nonyne, have been used with  $B_{10}H_{12}(Me_2S)_2$ ,  $B_{10}H_{12}(Ph_2S)_2$  and  $B_{10}H_{12}(Bu_2^tS)_2$ . Rate constants,  $\Delta H^{\neq}$ ,  $\Delta S^{\neq}$  and yields of ortho-carborane at different temperatures are given in Table 4.

The rate data indicate that the reaction of  $B_{10}H_{12}(Me_2S)_2$ with propargyl bromide is faster than for any other system. The activation entropies,  $\Delta S^{\neq}$ , have a rather wide range of values both positive and negative, which of course entirely depends on the nature of the transition state. The values of  $\Delta H^{\neq}$  reflect the nucleophilicites of the acetylenes. It is evident from Table 4 that for a given  $B_{10}H_{12}L_2$ , the less basic acetylenes, propargyl bromide and 2-butyne-1,4-diacetate, have higher  $\Delta H^{\neq}$  values than the more basic 1-nonyne. The data obtained in this work support the previously proposed mechanism [2].

# 4. Conclusions

The kinetic studies of the reactions of decaborane with different Lewis bases suggest that there are two major factors which influence the reaction rates and the activation parameters. These are the steric and electronic effects of the Lewis bases. More bulky or more electronegative groups attached to the central sulfur atom of the Lewis bases induce higher activation enthalpies for the reactions, resulting in slower reaction rates.

The kinetic studies of the reactions of decaborane–base adducts with acetylenes indicate that it is easier to lose bulky or electronegative ligands from the adduct. It is also evident that for a given adduct, the less basic acetylenes introduce higher activation enthalpies and higher yields of orthocarborane.

Considering the above factors, the most efficient way to achieve maximum yield of ortho-carborane, starting from decaborane and a Lewis base, followed by acetylene treatment, is to choose a relatively bulky and more basic Lewis base (L) to make the precursor  $(B_{10}H_{12}L_2)$ . The adduct

would then be treated with an acetylene that has no functional group attached to the C=C and has a low basicity.

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