253. The Relative Rates of Reaction of Decaborane with Some Nitriles and Sulphides.

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The rate of hydrogen evolution has been used to study the effect of concentration and temperature on the reaction of decaborane with acetonitrile and diethyl sulphide in dioxan solution. The rates of reaction of decaborane with derivatives of acetonitrile possessing $+I$ and $-I$ substituents are compared, and the effect of varying the availability of electrons on the nitrogen atom of the nitrile is discussed. Reactions of decaborane with several dialkyl sulphides and with diphenyl sulphide are examined.

NUCLEOPHILIC alkylation of decaborane by the action of organometallic reagents is known to involve the 6,9-boron atoms of the borane.[1] Attack at these electropositive positions with elimination of hydrogen explains the formation [2] of bisacetonitriledecaborane from decaborane and acetonitrile and the structure [3] of the product. Decaborane reacts with other electron donors, a common feature of which is the presence in the molecule of a Group V or VI element having a lone pair of electrons available for co-ordinate-bond formation. Products are obtained according to eqn. (1) in which M represents the electron-donor.[4,5] The structure of bis(dimethyl sulphide)decaborane has been shown

$$B_{10}H_{14} + 2M \longrightarrow H_2 + B_{10}H_{12}M_2 \quad \ldots \ldots \ldots \ldots (1)$$

recently [6] to be similar to that of the bisacetonitrile compound.

We have studied the reactions of decaborane with acetonitrile and diethyl sulphide in dioxan solution by measuring rate of evolution of hydrogen. The effect of varying the nucleophilic reactivity of the nitrile and the sulphide was examined by observing reactions between decaborane and derivatives of the electron donors possessing $+I$ and $-I$ substituents.

[1] Dunstan, R. L. Williams, and Blay, *J.*, 1960, 5012.
[2] Schaeffer, *J. Amer. Chem. Soc.*, 1957, **79**, 1006.
[3] Reddy and Lipscomb, *J. Chem. Phys.*, 1959, **31**, 610.
[4] Pace, J. Williams, and R. L. Williams, *J.*, 1961, 2196 and references therein.
[5] Graybill and Hawthorne, *J. Amer. Chem. Soc.*, 1961, **83**, 2673.
[6] Sand and Zalkin, Abs. of Papers, Internat. Congress of Crystallography, 1960.

EXPERIMENTAL

Materials.—Decaborane, purchased from the American Potash and Chemical Corporation, was recrystallised from hexane and stored *in vacuo* over calcium chloride. Dioxan was purified as described by Vogel.[7] Nitriles were distilled over phosphoric anhydride, in some cases under diminished pressure; to minimise polymerisation acrylonitrile and dinitriles were fractionally distilled without addition of phosphoric anhydride. Dialkyl sulphides were washed with 5% sodium hydroxide solution, then water, dried (CaCl₂), and distilled over sodium. Diphenyl sulphide was separated from sodium by filtration before distillation under diminished pressure.

Apparatus and Method.—The apparatus consisted of a 100-c.c. flask, immersed in a thermostat-bath and connected through a condenser to a gas-burette of 50 c.c. or 100 c.c. capacity, depending on the rate of gas evolution during an experiment. The condenser and burette were maintained at constant temperature (16° ± 0·05°). A levelling bulb and small mercury manometer were used to adjust the pressure of the gas in the burette to that of the atmosphere; the burette was emptied by a 3-way tap. Attached to a side-arm of the flask by a standard joint was a 40-c.c. cylindrical vessel with a bent neck; rotation about the joint enabled the nitrile or sulphide to be added to decaborane. Both reactants were dissolved in dioxan and the solutions were allowed to reach temperature equilibrium (30 min.) before mixing. Smooth evolution of hydrogen was ensured by adding a small quantity of porous pot. The rate of reaction was determined by measuring the volume of hydrogen evolved after convenient intervals of time. After allowance for the saturated vapour pressure of the solution, gas volumes were corrected to N.T.P. In a series of identical experiments the slope of the rate curve varied from the mean by ±4%; results obtained by shaking or vigorously stirring the solution fell within this range.

Reaction of Decaborane with Nitriles.—Decaborane (*ca.* 1·0 g.), accurately weighed in a small glass capsule and dissolved in anhydrous dioxan (15 c.c.), was treated with a 30% (w/v) solution of nitrile in anhydrous dioxan (15 c.c.) at 80° ± 0·05° and the rate of hydrogen evolution observed. In the case of acetonitrile, the % of decaborane reacted, calculated from the amount of hydrogen evolved (eqn. 1), was plotted against time for experiments in which the concentration of each reactant was varied in turn; rate of hydrogen evolution was also measured at 70° ± 0·05°.

Reaction of Decaborane with Sulphides.—Decaborane (*ca.* 1·0 g.) in anhydrous dioxan (15 c.c.) was treated with a 30% (v/v) solution of sulphide in anhydrous dioxan (15 c.c.) at 70° and the rate of hydrogen evolution observed. The effect of concentration on the reaction of decaborane with diethyl sulphide was investigated by varying the concentration of each in turn; the reaction was also studied at 80°.

Bis(diethyl sulphide)decaborane.—A solution of decaborane (3·69 g., 0·03 mole) and diethyl sulphide (6·28 g., 0·07 mole) in anhydrous ether (25 c.c.) was heated under reflux for 12 hr. On cooling, bis(diethyl sulphide)decaborane was obtained as colourless needles (3·03 g., 48%), m. p. 94° (Found: C, 32·3; H, 10·4; B, 35·7. Calc. for $C_8H_{32}B_{10}S_2$: C, 32·0; H, 10·7; B, 36·1%). Graybill and Hawthorne[5] give m. p. 90—91°.

RESULTS

Concentrations are expressed in mole l.⁻¹, rate of disappearance of decaborane as mole l.⁻¹ sec.⁻¹, and second-order rate constants as l. mole⁻¹ sec.⁻¹.

Reaction of Decaborane with Acetonitrile: Effect of Concentration and Temperature.—In the concentration range studied the rate of reaction of decaborane with acetonitrile was proportional to the concentration of acetonitrile for a given decaborane concentration, also to the concentration of decaborane at constant acetonitrile concentration. The reaction is thus of the first-order with respect to each reactant, the overall order being 2. Slopes obtained when the rate of hydrogen evolution reached a maximum steady value (after 15—30 min.) were taken as a measure of the rate of disappearance of decaborane according to eqn. 1 (M = MeCN); second-order rate constants (Table 1) were obtained by using the expression $-d[B_{10}H_{14}]/dt = k[B_{10}H_{14}][MeCN]$. The mean values of the second-order rate constants determined at 80° ($1·29 \times 10^{-5}$) and at 70° ($5·40 \times 10^{-6}$) led to an activation energy of $21·0 \pm 1·0$ kcal. mole⁻¹.

Nucleophilic Reactivity of Nitriles.—Second-order rate constants for reactions of a number of alkyl cyanides with decaborane, measured by rate of hydrogen evolution, are shown in Table 2.

[7] Vogel, " A Textbook of Practical Organic Chemistry," Longmans, London, 2nd edn.

TABLE 1.

Second-order rate constants for the reaction of acetonitrile with decaborane in dioxan
at 80° (volume of solution at 80° = 32 c.c.).

[MeCN]	2·980	2·980	2·980	1·192	0·5959
[$B_{10}H_{14}$]	0·03171	0·1285	0·2568	0·2553	0·2563
$-10^6 d[B_{10}H_{14}]/dt$	1·212	4·739	9·465	4·055	2·087
$10^5 k$	1·283	1·238	1·237	1·332	1·366

In the series malononitrile to pimelonitrile, rate of disappearance of decaborane was
calculated in accordance with the reaction:

$$x B_{10}H_{14} + x NC \cdot [CH_2]_n \cdot NC \longrightarrow x H_2 + (NC \cdot [CH_2]_n \cdot CN, B_{10}H_{12})_x$$
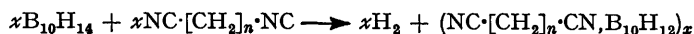
Evolution of hydrogen from the reaction of decaborane with nitriles in dioxan was accom-
panied by formation of pale yellow to dark brown products. Evaporation of the final solution
usually gave intractable oils and gels. The product from the reaction of adiponitrile with
decaborane was an orange solid, insoluble in common organic solvents and readily hydrolysed
to boric acid. The possibility that halogen-substituted derivatives of acetonitrile reacted with
decaborane to form B–C in addition to B–N bonds was considered, but there was no evidence
of hydrogen halide formed under the conditions used.

Anomalous results were obtained with nitriles having additional groups capable of indepen-
dent reaction with decaborane. Thus o-nitrobenzonitrile (k^{80} 3·57 × 10^{-4}) and p-hydroxy-
benzonitrile (k^{80} 1·15 × 10^{-4}) reacted very much faster than benzonitrile (k^{80} 9·07 × 10^{-6}).
Presumably o-nitrobenzonitrile may undergo reduction to an amine which reacts with deca-
borane to liberate hydrogen.[8] The occurrence of an unusual reaction was also indicated by
an immediate green-brown coloration when decaborane and o-nitrobenzonitrile were mixed in
dioxan; there was some indication that heat was evolved. In the case of p-hydroxybenzo-

TABLE 2.

Second-order rate constants for the reaction of decaborane with nitriles possessing
$+I$ and $-I$ substituents in dioxan at 80° (volume of solution at 80° = 32 c.c.).

R in RCN	[RCN]	[$B_{10}H_{14}$]	$-10^6 d[B_{10}H_{14}]/dt$	$10^6 k$
Me	2·980	0·2568	9·465	12·4
Et	2·221	0·2568	7·865	13·8
Pr^n	1·800	0·2548	6·780	14·8
Pr^i	1·748	0·2563	6·320	14·1
Bu	1·507	0·2568	6·755	17·5
$C_{12}H_{25}$	0·8861	0·2975	4·078	15·5
Cl·CH_2	2·469	0·2563	2·347	3·71
Cl·$[CH_2]_2$	1·998	0·2558	3·411	6·67
Cl·$[CH_2]_3$	1·692	0·2558	4·476	10·3
Cl_2CH	1·969	0·2558	0·4487	0·891
Br·$[CH_2]_2$	1·887	0·2591	3·881	7·94
Br·$[CH_2]_3$	1·589	0·2591	3·943	9·58
Br_2CH	1·829	0·2568	2·365	5·04
MeO·CH_2	2·080	0·2568	2·109	3·95
EtO_2C·CH_2	1·469	0·2563	2·532	6·73
NC·CH_2	1·427	0·2586	0·5405	1·46
NC·$[CH_2]_2$	2·421	0·2563	9·705	15·6
NC·$[CH_2]_3$	1·621	0·2558	9·525	23·0
NC·$[CH_2]_4$	1·268	0·2555	10·92	33·7
NC·$[CH_2]_5$	1·201	0·2517	11·38	37·6

nitrile it is likely that both functional groups interact with decaborane to produce hydrogen.
Slow hydrogen evolution (k^{80} 6·84 × 10^{-6}) was observed in interaction of acrylonitrile with
decaborane but the rapid formation of a voluminous precipitate suggested that the nitrile
probably underwent extensive polymerisation simultaneously.

Reaction of Decaborane with Diethyl Sulphide: Effect of Concentration and Temperature.—By
varying the concentration of each reactant in turn it was established that the reaction between
decaborane and diethyl sulphide in dioxan is first-order with respect to each compound. Rate

[8] Beachell and Dietrich, *J. Amer. Chem. Soc.*, 1961, **83**, 1347.

of hydrogen evolution was used to measure the rate of disappearance of decaborane according to eqn. 1 (M = Et$_2$S); second-order rate constants (Table 3) were calculated as usual. An activation energy of 19·4 ± 1·0 kcal. mole^{-1} was calculated from the mean values of the second-order rate constants at 70° (6·30 × 10^{-5}) and at 80° (14·1 × 10^{-5}).

TABLE 3.

Second-order rate constants for the reaction of diethyl sulphide with decaborane in dioxan at 70° (volume of solution at 70° = 31·6 c.c.).

[Et$_2$S]	1·469	1·469	1·469	0·5874	4·403
[B$_{10}$H$_{14}$]	0·08071	0·2616	0·7732	0·2610	0·2595
−10^{5}d[B$_{10}$H$_{14}$]/dt	0·7310	2·395	7·320	1·024	6·820
10^5k	6·165	6·232	6·445	6·679	5·969

Nucleophilic Reactivity of Sulphides.—Second-order rate constants for the reaction of decaborane with several dialkyl sulphides and diphenyl sulphide in dioxan at 70° are presented in Table 4.

TABLE 4.

Second-order rate constants for the reaction of decaborane with dialkyl sulphides and diphenyl sulphide in dioxan at 70°.

R in R$_2$S	[R$_2$S]	[B$_{10}$H$_{14}$]	−10^{6}d[B$_{10}$H$_{14}$]/dt	10^5k
Et	1·469	0·2616	23·95	6·23
Pr	1·089	0·2610	12·22	4·30
Bu	0·9072	0·2616	12·01	5·06
Ph	0·7423	0·2613	0·9965	0·514

DISCUSSION

The rate of reaction between decaborane and an aliphatic nitrile is related to the availability of electrons on the nitrogen atom of the latter. In general, +I substituents increase and −I substituents decrease the reactivity of acetonitrile derivatives toward decaborane (Table 2). An analogous relation has been reported [9] for the reactions of alcohols with decaborane, the rate of alcoholysis increasing with an increase in the electronegativity of the hydroxyl-oxygen. A similar increase in rate with an increase in electron density has been observed for the reaction of aromatic amines with decaborane.[8]

Malononitrile reacts very slowly with decaborane. It is possible that in intermediates of the type NC·[CH$_2$]$_n$·CN(B$_{10}$H$_{12}$,NC·[CH$_2$]$_n$·CN)$_x$ the nitrile group exhibits reduced nucleophilic reactivity owing to electron-withdrawal by the decaborane, the effect being greater for low values of n. Increasing chain length and a greater tendency for both functional groups to react with decaborane probably explain the relatively high rate constants for glutaronitrile and its higher homologues.

By analogy with the formation of bis(dimethyl sulphide)decaborane [6] reactions of other dialkyl sulphides with decaborane probably involve attack by the electronegative sulphur atom at an electropositive site in decaborane; the reactions should be favoured by substituents which increase the availability of electrons on the sulphur atom. However, the order of reactivity of the dialkyl sulphides is not regular, suggesting that the inductive effect of the alkyl groups is not the only controlling factor. For diphenyl sulphide mesomeric and steric effects may influence the reaction rate.

The structures of bisacetonitriledecaborane [3] and bis(dimethyl sulphide)decaborane [6] indicate that the reactions involve bond formation between nitrogen or sulphur and the 6,9-boron atoms of decaborane; bridge protons are redistributed and hydrogen is eliminated. Although diethyl sulphide reacts faster than acetonitrile (k_{Et_2S}/k_{MeCN}, 11·7 at 70°, 10·9 at 80°) the activation energies are comparable and each reaction might well proceed by the same mechanism. It has been suggested [8] that all reactions yielding compounds of the type B$_{10}$H$_{12}$M$_2$ may be regarded as acid–base interactions, decaborane

[9] Beachell and Schar, *J. Amer. Chem. Soc.*, 1958, **80**, 2943.

acting as an acid,[10] and the electron-donors exhibiting basic character. The reactions of decaborane with pyridine [11] and with aromatic amines [8] have been expressed as $B_{10}H_{14} + M \xrightarrow{\text{Fast}} B_{10}H_{14}M \xrightarrow[\text{Slow}]{+M} B_{10}H_{12}M_2 + H_2$, and there is spectroscopic evidence [8,12] for the existence of an intermediate of the type $B_{10}H_{14}M$. Although the kinetics of reactions of decaborane with acetonitrile and diethyl sulphide have not been examined in detail here, the results are not consistent with such a mechanism. An alternative scheme is tentatively suggested for reactions involving acetonitrile and diethyl sulphide:

$$B_{10}H_{14} + M \underset{\text{Fast}}{\rightleftharpoons} B_{10}H_{14}M \xrightarrow{\text{Slow}} H_2 + B_{10}H_{12}M \xrightarrow[\text{Fast}]{+M} B_{10}H_{12}M_2$$
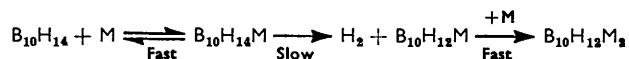
The intermediate $B_{10}H_{14}M$, formed in a rapidly established equilibrium between decaborane and the electron donor, decomposes in a rate-determining step, liberating hydrogen and yielding a reactive intermediate $B_{10}H_{12}M$ which is converted rapidly into $B_{10}H_{12}M_2$.

[10] Guter and Schaeffer, *J. Amer. Chem. Soc.*, 1956, **78**, 3456.
[11] Fetter and Burkardt, Abs. 135th Amer. Chem. Soc. Meeting, Boston, 1959.
[12] Hawthorne, Pitochelli, Strahm, and Miller, *J. Amer. Chem. Soc.*, 1960, **82**, 1825.