Possible Mechanisms of the Reaction Between Tetrahydroborate and Hydrogen Ions: A Permutational Analysis

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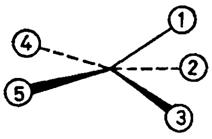
A detailed permutational analysis of the reaction sequence $[BH_4]^- + H^+ \longrightarrow BH_5 \longrightarrow BH_3 + H_2$ leads to the suggestion that the reaction, in aqueous solution, could proceed *via* a rigid C_s intermediate BH_5 having a kind of H_2 subunit as potentially evolving molecular hydrogen, in agreement with previous quantum-mechanical calculations. On the other hand, the anhydrous reaction $Na[BH_4] + H_2SO_4$ could proceed *via* a trigonal-bipyramidal intermediate with edge attack of the $[BH_4]^-$ tetrahedral structure, followed by axial–equatorial loss from the trigonal bipyramid. Finally, it is likely that the anhydrous reaction $Na[BH_4] + HF$ proceeds *via* a non-rigid BH_5 intermediate of undetermined structure.

THE literature is replete with experimental and theoretical evidence supporting the existence of BH_5 as a short-lived intermediate in the reaction $[BH_4]^- + H^+ \longrightarrow BH_3 + H_2$.[1,2] However, data on the structure and stereochemical properties of this intermediate are not very numerous. Recent quantum-mechanical calculations by Pepperberg *et al.*[3] led to the suggestion that the optimal geometry for BH_5, at least in aqueous solution, is a structure (Z) having C_s symmetry in which two hydrogen atoms (4 and 5) occupy a kind of 'H_2 subunit'[3] giving rise naturally to molecular hydrogen when BH_5 decomposes to the reaction products. This conclusion is in agreement with experimental data in aqueous solution[3] (see below), but it is not established that it can be extrapolated to other experimental conditions (*e.g.* the reaction of $Na[BH_4]$ with H_2SO_4 or HF in anhydrous conditions[1d]).



(Z)

Moreover, in reactions involving five-co-ordinate intermediates, three types of structure can be envisaged for the latter: the C_s structure mentioned above, the C_{4v} square pyramid, and the D_{3h} trigonal bipyramid. The aim of this paper is to give a permutational analysis of the reaction sequence $[BH_4]^- + H^+ \longrightarrow$ five-co-ordinate intermediate $\longrightarrow BH_3 + H_2$ as a function of the structure and the stereochemical features of the intermediate BH_5. Comparison of the results with labelling experiments[1] gives some further insight into the mechanism of the reaction.

There are several types of symmetry approach to the elucidation of problems in dynamic stereochemistry. (*a*) Methods based on Longuet-Higgins groups are relevant in the classification of transitions in rovibronic spectra when quantum-mechanical tunneling is present.[4] (*b*) Methods based on transition-state selection rules by which some symmetries of transition states may be ruled out.[5] These rules are essentially relevant for elementary paths including an initial state (reactants), a transition state, and a final state (products). These group-theoretical rules provide some insight into the structure of the transition state and can lead to a better choice of the reaction paths that are worthwhile analyzing by quantum-mechanical calculations.[5a] (*c*) Methods based on a study of the permutational character of a reaction or of a sequence of reactions when short-lived intermediates (not transition states) are present. This type of approach allows one to find all the *a priori* possible stereochemical changes of these reactions or sequences of reactions, according to the symmetry of the initial, intermediate, and final potential minima, without referring to transition states which cannot be approached by this method. Indeed a given reaction path is characterized by a given permutational character, but a given permutational character does not characterize the reaction path.[6]

My analysis is based on approach (*c*) which was developed by Klemperer[6] and other workers.[7-9, 10] The paper is divided into three parts. The first section is devoted to the general qualitative principle of the method and to its application to the reaction $[BH_4]^- + H^+ \longrightarrow BH_3 + H_2$. The results of this analysis are discussed from a chemical point of view only. Next, the group theoretical fundamentals of the method, on which the results of section 1 are outlined, and finally, some calculation details are given.

RESULTS AND DISCUSSION

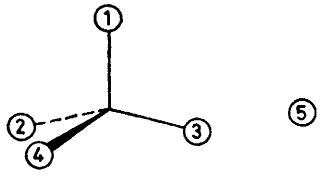
(1) *From the Permutational Character of the Reaction* $[BH_4]^- + H^+ \longrightarrow BH_3 + H_2$ *to its Possible Mechanisms.*—(*a*) *The concept of modes and product of modes.* A mode of reactions (or set of non-differentiable reactions in the nomenclature of Klemperer[6]) is a set of reactions which are undistinguishable because they are symmetry equivalent, so that they occur with the same rate constant, or they are characterized by the same initial and final configuration state. The number of modes is the maximum number of experimentally observable distinguishable stereochemical changes of a given reaction. Of course, several different reaction *mechanisms* (energy profiles) may belong to the same mode and be therefore experimentally undistinguishable because they are characterized by the same initial and final configuration state.

Consider the skeletal labelling of the set of reactants $[BH_4]^- + H^+$ (V) and the set of products $BH_3 + H_2$

(W). Using the procedure of the following section [6] it is possible to show that there are only two distinguishable reaction modes relating the set of reactants (V) to the set of products (W). These modes are depicted in Table 1. M_i^{WV} symbolizes the mode number i for the reaction from (V) to (W).[6] The connectivity δ_i^{WV} (refs. 6 and 11) is the number of configurations of (W) which can be generated from the configuration (V) by application of the mode M_i^{WV}. The configurations of (W) are symbolized by the labels, in increasing order, of the two nuclei in molecular hydrogen; for instance, configuration 45 is that in which the three hydrogen atoms of BH_3 are labelled 1, 2, and 3 and the two hydrogen atoms of H_2 are labelled 4 and 5. This configuration of (W) is shown above.

TABLE 1

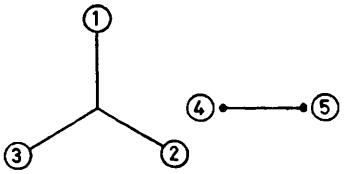
Mode	Connectivity	Configurations generated
M_1^{WV}	4	15, 25, 35, 45
M_2^{WV}	6	12, 13, 14, 23, 24, 34



(V)

Clearly mode M_1^{WV} includes the four symmetry-equivalent configuration conversions from (V) to (W) in which the proton H^+ (nucleus labelled 5 above) of the reactants (V) enters the molecular hydrogen in the products (W); in contrast, the mode M_2^{WV} includes the six symmetry-equivalent configuration conversions in which H^+ enters the BH_3 molecule. Suppose that we label isotopically nucleus 5, *i.e.* we examine the reaction $[BH_4]^- + D^+$. From Table 1 it is seen that, if the reaction obeys the permutational character of M_1^{WV}, the reaction products are BH_3 and HD, since in all the configurations generated by that mode nucleus 5 is contained in molecular hydrogen. On the other hand, if the reaction obeys the permutational character of M_2^{WV}, the reaction products are BDH_2 and H_2.

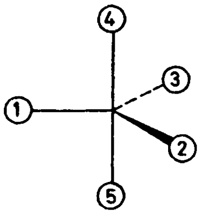
Consider now a reaction sequence of the type (V) ⟶ (Q) ⟶ (W), in which (Q) is the short-lived undetected intermediate BH_5. It is easy to see that the permutational character of this sequence depends on (*i*) the symmetry of the intermediate (Q) [extended symmetry if the intermediate is non-rigid—see section 3(*c*)],[4] (*ii*) the reaction mode M_j^{QV} by which the reactants (V) are transformed into the intermediate (Q), and (*iii*) the reaction mode M_k^{WQ} by which the intermediate (Q) is transformed into the products (W). When the reaction (V) ⟶ (Q) occurs according to the mode M_j^{QV} and when the reaction (Q) ⟶ (W) occurs according to the mode M_k^{WQ}, then the reaction sequence (V) ⟶ (Q) ⟶ (W) occurs according to the product $M_k^{WQ}M_j^{QV}$. It can be shown mathematically [see section 3(*a*)] that such a product of modes always results in a ***linear combination*** of the reaction modes M_i^{WV}. In such a linear combination each mode M_1^{WV} and M_2^{WV} appears with a given weight or probability, p_1 and p_2 respectively, depending on the symmetry of the intermediate (Q), on M_j^{QV}, and on M_k^{WQ}. The resulting product $M_k^{WQ}M_j^{QV}$ is then merely characterized by the permutational character defined by the set of numbers $(p_1, p_2)_Q^{WV}$. Therefore, if a mode sequence $M_k^{WQ}M_j^{QV}$ is such that the probability of occurrence of M_1^{WV} is p_1 and that of M_2^{WV} is p_2, then the reaction $[BH_4]^- + D^+$ must provide $100p_1$ mol % HD and $100p_2$ mol % H_2. This result is of course only valid when isotope effects are negligibly small and isotopic labelling does not affect the symmetry of the molecular skeleton, *i.e.* the mode concept remains physically meaningful.



(W)

In subsequent sections I establish the permutational character (p_1, p_2) for the sequences generated from all the possible products of modes $M_k^{WQ}M_j^{QV}$, the intermediate (Q) being the BH_5 molecule with D_{3h}, C_{4v}, or C_s structure. The effect of eventual non-rigidity of the intermediate is also examined. From the calculated permutational characters I derive the expected mol fractions of evolving H_2 and HD.

(*b*) *Trigonal bipyramid* D_{3h} *as intermediate.* The sites of the trigonal-bipyramidal intermediate (Q)=(X) are numbered as shown. The modes M_j^{XV} of the reaction (V) ⟶ (X) are given in Table 2, together with their connectivity and an example of mechanism (which need not be unique for a given mode). M_1^{XV} differs only from M_3^{XV} in that the latter corresponds from a permu-



(X)

TABLE 2

Mode	Connectivity	Example of mechanism (type of attack on the tetrahedron)
M_1^{XV}	4	Facial
M_2^{XV}	6	Edge
M_3^{XV}	4	Facial combined with exchange of two ligands
M_4^{XV}	6	Edge combined with exchange of two ligands

tational point of view to the former combined with a reflection symmetry operation [see section 3(*b*)], *e.g.* permutation of two equatorial ligands of the trigonal bipyramid. A similar relation exists between M_2^{XV} and M_4^{XV}. It is intuitively easy to see that the reaction mode M_1^{XV} must have a connectivity of 4 since there are four symmetry-equivalent faces in the tetrahedron $[BH_4]^-$ that can be attacked with equal probability by H^+. The modes M_k^{WX} of the reaction (X) → (W) are given in Table 3.

TABLE 3

Mode	Connectivity	Example of mechanism
M_1^{WX}	1	Diaxial loss
M_2^{WX}	3	Diequatorial loss
M_3^{WX}	6	Axial–equatorial loss

From the data of Tables 2 and 3, using the procedure explained in section 1(*a*) and detailed mathematically in 3(*a*), we can calculate permutational characters of all the possible mode products $M_k^{WX}M_j^{XV}$. These are given in Table 4 together with the theoretical mol fractions of HD and H_2 they give rise to. From Table 4 it is seen that the permutational characters of the mode products $M_k^{WX}M_1^{XV}$ and $M_k^{WX}M_3^{XV}$ on one hand, and of $M_k^{WX}M_2^{XV}$ and $M_k^{WX}M_4^{XV}$ on the other, are identical. This is due to the special relation within the pairs of modes M_1^{XV}, M_3^{XV} and M_2^{XV}, M_4^{XV} mentioned above.

TABLE 4

M_k^{WX}	M_j^{XV}	$(p_1, p_2)_X^{WV}$	Mol % HD	Mol % H_2
M_1^{WX}	M_1^{XV}	$(1, 0)_X^{WV}$	100	0
M_1^{WX}	M_2^{XV}	$(0, 1)_X^{WV}$	0	100
M_1^{WX}	M_3^{XV}	$(1, 0)_X^{WV}$	100	0
M_1^{WX}	M_4^{XV}	$(0, 1)_X^{WV}$	0	100
M_2^{WX}	M_1^{XV}	$(0, 1)_X^{WV}$	0	100
M_2^{WX}	M_2^{XV}	$(\frac{2}{3}, \frac{1}{3})_X^{WV}$	66.67	33.33
M_2^{WX}	M_3^{XV}	$(0, 1)_X^{WV}$	0	100
M_2^{WX}	M_4^{XV}	$(\frac{2}{3}, \frac{1}{3})_X^{WV}$	66.67	33.33
M_3^{WX}	M_1^{XV}	$(\frac{1}{2}, \frac{1}{2})_X^{WV}$	50	50
M_3^{WX}	M_2^{XV}	$(\frac{1}{3}, \frac{2}{3})_X^{WV}$	33.33	66.67
M_3^{WX}	M_3^{XV}	$(\frac{1}{2}, \frac{1}{2})_X^{WV}$	50	50
M_3^{WX}	M_4^{XV}	$(\frac{1}{3}, \frac{2}{3})_X^{WV}$	33.33	66.67

The way in which non-rigidity of the intermediate can be taken into account is explained in section 3(*c*). I therefore only give the result here. If the trigonal bipyramid rearranges rapidly according to the inversion mode (P_5 in the notation of Gielen and Van Lautem [10] or M_3 in the notation of Musher [12]), the permutational characters are the same as for the rigid trigonal bipyramid. However, if the intermediate rearranges rapidly according to any other mode the resulting permutational character is $\left(\frac{2}{5}, \frac{3}{5}\right)_{X(NR)}^{WV}$ where X(NR) means ' non-rigid X '. The resulting mol fractions of evolving molecular hydrogen are 40% HD and 60% H_2.

(*c*) *Square pyramid C_{4v} as intermediate.* The procedure is exactly the same as for the trigonal bipyramid. The skeletal sites of the square pyramid are labelled as in (Y). The modes for the reaction $[BH_4]^- + H^+ \longrightarrow BH_5(C_{4v})$, (V) → (Y), are given in Table 5, those for $BH_5(C_{4v}) \longrightarrow BH_3 + H_2$, (Y) → (W), in Table 6. From the data in Tables 5 and 6, all the possible permutational characters for the reaction sequence (V) → (Y) → (W) can be deduced. These are given in Table 7, together with the corresponding theoretical mol fractions of HD and H_2. Note from Table 7 that for fixed M_j^{YV} both types of dibasal losses (M_2^{WY} or M_3^{WY}) lead to the same permutational characters for the sequence (V) → (Y) → (W).

TABLE 5

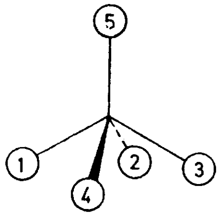
Mode	Connectivity	Example of mechanism
M_1^{YV}	6	Apical attack
M_2^{YV}	12	Basal attack
M_3^{YV}	12	M_2^{YV} combined with a reflection

TABLE 6

Mode	Connectivity	Example of mechanism
M_1^{WY}	4	Apical–basal loss
M_2^{WY}	4	Dibasal *cis* loss
M_3^{WY}	2	Dibasal *trans* loss

TABLE 7

M_k^{WY}	M_j^{YV}	$(p_1, p_2)_Y^{WV}$	Mol % HD	Mol % H_2
M_1^{WY}	M_1^{YV}	$(1, 0)_Y^{WV}$	100	0
M_1^{WY}	M_2^{YV} or M_3^{YV}	$(\frac{1}{4}, \frac{3}{4})_Y^{WV}$	25	75
M_2^{WY}	M_1^{YV}	$(0, 1)_Y^{WV}$	0	100
M_2^{WY}	M_2^{YV} or M_3^{YV}	$(\frac{1}{2}, \frac{1}{2})_Y^{WV}$	50	50
M_3^{WY}	M_1^{YV}	$(0, 1)_Y^{WV}$	0	100
M_3^{WY}	M_2^{YV} or M_3^{YV}	$(\frac{1}{2}, \frac{1}{2})_Y^{WV}$	50	50



(Y)

To study the influence of a rapidly rearranging square pyramid on these permutational characters it should be noted that there are two types of permutational-rearrangement modes among the seven possible ones for this polytope.[10] The first type of mode leaves the apical ligand unchanged; using the procedures of section 3(*c*), it can be shown that if the C_{4v} rearranges rapidly according to one of these modes the permutational characters for the sequence (V) → (Y) → (W) are the same as for the rigid square pyramid. The second type of mode for (Y) is that in which the apical ligand is brought into the basal position; for this case the permutational character is the same as for a non-rigid trigonal bipyramid [see relation (14)], namely $\left(\frac{2}{5}, \frac{3}{5}\right)_{Y(NR)}^{WV}$, where Y(NR) means ' non-rigid Y ', for any M_k^{WY} and M_j^{YV}. That the permutational characters are the same for the non-rigid square pyramid and trigonal bipyramid is not surprising since scrambling of all the positions in the respective skeleta leads to the consequence that all the configurations of $BH_3 + H_2$ are generated with the same probability; hence, since only four configurations among the ten possible have the hydrogen atom labelled 5 in the evolving molecular hydrogen, it is normal to expect a mol fraction of 40% HD in isotopic-labelling experiments with D^+.

(*d*) *The C_s intermediate.* The intermediate described in this section is that depicted as (Z). The modes for the reaction (V) $\longrightarrow$ (Z) are given in Table 8, from which it is seen that the five modes are essentially subdivided into two types: those in which H^+ enters the H_2 subunit and those in which H^+ does not. The modes for the reaction (Z) $\longrightarrow$ (W) are given in Table 9. The modes of reaction (Z) $\longrightarrow$ (W) are essentially subdivided into three types, according to the number of atoms of the H_2 subunit in the C_s intermediate (Z) that are present in evolving molecular hydrogen. Of course, it seems reasonable to consider the H_2 subunit in the C_s intermediate as the potentially evolving molecular hydrogen, so that the mode M_1^{WZ} is probably the most likely permutational character for the reaction (Z) $\longrightarrow$ (W). All the possible permutational characters for the reaction sequence (V) $\longrightarrow$ (Z) $\longrightarrow$ (W) are given in Table 10. From Table 10 it appears that only three types of permutational character are possible; assuming that M_1^{WZ} is the most likely, the number of permutational characters reduces to two according to whether the group D^+ enters the H_2 subunit (M_1^{ZV} and M_2^{ZV}) or not (M_3^{ZV} to M_5^{ZV}), giving rise respectively to 100% HD and 100% H_2.

TABLE 8

Mode	Connectivity	Characterization of the mode (in terms of whether H^+ enters the H_2 subunit)
M_1^{ZV}	24	Yes
M_2^{ZV}	24	Yes
M_3^{ZV}	24	No
M_4^{ZV}	24	No
M_6^{ZV}	24	No

TABLE 9

Mode	Connectivity	Characterization of the mode (atoms of the subunit in evolving H_2)
M_1^{WZ}	1	Both
M_2^{WZ}	2	One
M_3^{WZ}	2	One
M_4^{WZ}	2	One
M_5^{WZ}	2	None
M_6^{WZ}	1	None

TABLE 10

Permutational character of $M_k^{WZ}M_j^{ZV}$

k	j	Permutational character	mol % HD	mol % H_2
1	1	(1, 0)	100	0
	2	(1, 0)	100	0
	3	(0, 1)	0	100
	4	(0, 1)	0	100
	5	(0, 1)	0	100
2	1	$(\frac{1}{2}, \frac{1}{2})$	50	50
	2	$(\frac{1}{2}, \frac{1}{2})$	50	50
	3	$(\frac{1}{2}, \frac{1}{2})$	50	50
	4	$(\frac{1}{2}, \frac{1}{2})$	50	50
	5	(0, 1)	0	100
3	1	$(\frac{1}{2}, \frac{1}{2})$	50	50
	2	$(\frac{1}{2}, \frac{1}{2})$	50	50
	3	(0, 1)	0	100
	4	(0, 1)	0	100
	5	(1, 0)	100	0
4	1	$(\frac{1}{2}, \frac{1}{2})$	50	50
	2	$(\frac{1}{2}, \frac{1}{2})$	50	50
	3	$(\frac{1}{2}, \frac{1}{2})$	50	50
	4	$(\frac{1}{2}, \frac{1}{2})$	50	50
	5	(0, 1)	0	100
5	1	(0, 1)	0	100
	2	(0, 1)	0	100
	3	$(\frac{1}{2}, \frac{1}{2})$	50	50
	4	$(\frac{1}{2}, \frac{1}{2})$	50	50
	5	(1, 0)	100	0
6	1	(0, 1)	0	100
	2	(0, 1)	0	100
	3	(1, 0)	100	0
	4	(1, 0)	100	0
	5	(0, 1)	0	100

The permutational characters of the reaction sequence (V) $\longrightarrow$ (Z) $\longrightarrow$ (W), with (Z) rearranging immeasurably rapidly on the observational time scale, is more tedious to determine; indeed the great number (64) of possible rearrangement modes for the C_s intermediate makes a systematic study rather lengthy and would probably lead to poorly representative results. We therefore look for the influence of non-rigidity at the C_s intermediate under the following assumptions. If the C_s structure is the actual intermediate it seems reasonable to admit that the H_2 subunit gives rise to the evolving molecular hydrogen, *i.e.* it is assumed that the actual permutational character of the reaction (Z) $\longrightarrow$ (W) is defined by the mode M_1^{WZ}; this is in agreement with previous calculations.[3] The second assumption is a consequence of the first: if the H_2 subunit is the potentially evolving molecular hydrogen, the presence of nucleus 5 (*i.e.* the deuterium atom) in the latter depends essentially on two factors: (*i*) does nucleus 5 enter the subunit or not?, and (*ii*) is there a rearrangement in (Z) leading to a scrambling of the ligands of the triplet with those of the H_2 subunit? This means that for a given sequence $M_k^{WZ}M_j^{ZV}$ the permutational character obtained is the same if the intermediate is rigid or undergoes rapid rearrangement within the triplet and/or within the H_2 subunit.

Using a similar procedure as for the trigonal bipyramid and the square pyramid [see sections 3(*b*) and 3(*c*)], it can be shown that the permutational character of the sequence (V) $\longrightarrow$ non-rigid (Z) $\longrightarrow$ (W) is $\left(\frac{2}{5}, \frac{3}{5}\right)_{Z(NR)}^{WV}$ if (Z) rearranges rapidly according to modes in which at least one H atom of the H_2 subunit is transferred to a position of the triplet and if the actual permutational character of the reaction (Z) $\longrightarrow$ (W) is determined by the mode M_1^{WZ} (H_2 subunit $\longrightarrow$ molecular hydrogen). Further discussion on the influences of the non-rigidity of (Z) on the permutational character of the reaction (V) $\longrightarrow$ (W) is somewhat tedious.

(*e*) *Discussion.* The literature provides interesting labelling experiments[1] for the reaction $[BH_4]^- + H^+ \longrightarrow BH_3 + H_2$. The isotopic composition of the evolving molecular hydrogen depends strongly on the reaction conditions, according to the results presented in Table 11. Let me point out immediately that my model fails to predict the formation of small amounts of D_2 (maximum 3%); this discrepancy is essentially due to the fact that at pH 10 the reaction $[BH_4]^- + D^+ \longrightarrow BDH_4$ is slightly reversible:[1,3] BDH_4 can[1-3] lose H^+

and form $[BDH_3]^-$, which *via* the reaction $[BDH_3]^- + D^+$ can generate D_2; the probability of exchange of D^+ with H^+ *versus* formation of molecular hydrogen is $<1:10$, but not negligible. Because of this, and also because of the uncertainty of the isotope effect in the different reaction steps, a difference of 4—8% between experimental and calculated mol fractions is acceptable. Note in addition that all the arguments presented so far can be applied to the reaction $[BD_4]^- + H^+$, the roles of H and D being simply reversed; however, the mol percentage of H_2 in the reactions $[BH_4]^- + D^+$ and $[BD_4]^- + H^+$ is always slightly larger than that of D_2 in the reaction $[BD_4]^- + H^+$ and $[BH_4]^- + D^+$ respectively; Pepperberg *et al.*[3] consider this to be a measure of the extent of exchange with solvent prior to hydrolysis.

TABLE 11

Ref.	Conditions	Reaction	mol % H_2	mol % HD	mol % D_2
1*a*, 1*b*, 3	Aqueous solution	$[BD_4]^- + H^+$	3.1	95.6	1.3
	Aqueous solution, 0 °C	$[BH_4]^- + D^+$	3.9	94.9	1.1
	Aqueous solution, 50 °C	$[BH_4]^- + D^+$	3.0	95.6	1.4
1*d*	Anhydrous	$Na[BH_4] + D_2SO_4$	67.0	32.5	0.5
	Anhydrous	$Na[BD_4] + H_2SO_4$	2.1	38.5	59.4
	Anhydrous	$Na[BH_4] + DF$	57.7	39.6	2.7
	Anhydrous	$Na[BD_4] + HF$	4.5	37.9	57.6

Taking these restrictions into account, we can now turn to an analysis of the experimental results (Table 11). For the reaction in aqueous solution, the presence of 95.6% of HD can be interpreted in terms of the permutational character (1, 0). As mentioned previously[3] and as confirmed by this permutational analysis, the actual reaction sequence cannot involve a rapidly rearranging intermediate. Among the possible sequences satisfying the observed permutational character, let us consider facial attack to a trigonal bipyramid followed by diaxial loss of H_2, apical attack to a square pyramid followed by an apical–basal loss, and attack of D^+ to the H_2 subunit of the C_s intermediate, followed by loss of the H_2 subunit. The latter sequence has been shown[3] to be energetically the most favourable one. The reaction $Na[BH_4] + H_2SO_4$ in anhydrous conditions is somewhat more difficult to discuss because there is a non-negligible discrepancy between the mol percentages of H_2,HD, and D_2 obtained for the reactions $Na[BD_4] + H_2SO_4$ and $Na[BH_4] + D_2SO_4$ respectively (see Table 11). Consequently, it is difficult to find out whether the actual permutational character of the reaction is $\left(\frac{1}{3}, \frac{2}{3}\right)$ or $\left(\frac{2}{5}, \frac{3}{5}\right)$. Among the possible interpretations, *e.g.* the black box 'isotopic effect', I suggest the following. The labelling experiment was claimed to be performed with 100% D_2SO_4[1a]; however, the isotopic purity of deuteriated $Na[BH_4]$ was not mentioned. Therefore, the experimental mol ratios of the reaction $Na[BH_4] + D_2SO_4$ are to be trusted more than those of $Na[BD_4] + H_2SO_4$, and this leads to the conclusion that for the latter reaction the experimental mol fractions of H_2 and HD are too high and that of D_2 is too low. Consequently, I believe that it is not unreasonable that the effective mol percentage of D_2 would be $>60\%$ and approach 67% if $Na[BD_4]$ were isotopically pure, and hence the reaction $Na[BD_4] + H_2SO_4$ has the permutational character $\left(\frac{1}{3}, \frac{2}{3}\right)$, like $Na[BH_4] + D_2SO_4$. In any case, it is unlikely that these two reactions have different permutational characters. If this interpretation is correct, Tables 2—4 show that the most likely mechanism for the reaction $Na[BH_4] + H_2SO_4$ is edge attack of H^+ to a trigonal bipyramid followed by axial–equatorial loss of H_2.

In view of this discussion, it is perhaps somewhat strange that such a discrepancy does not appear for the reaction $Na[BH_4] + HF$, especially if DF is isotopically pure. However, since the experimental ratios found for the reactions $Na[BD_4] + HF$ and $Na[BH_4] + DF$ are close to the calculated ratio of 40 : 60, the permutational character of both reactions can safely be considered as $\left(\frac{2}{5}, \frac{3}{5}\right)$. This conclusion is in agreement with the early suggestion[1d] that the reaction proceeds through a non-rigid five-co-ordinate intermediate the structure of which cannot be determined otherwise than by calculations.

The aim of this paper was to show the efficiency of a quite new type of reaction-mechanism analysis which, of course, does not establish unambiguously an actual path, but rather excludes a lot of them. I believe that the methods of permutational analysis, quantum-mechanical calculations, and experimental labelling should be used as independent but complementary tools in the elucidation of reaction mechanisms.

(2) *Theory*.—The permutational character of a reaction sequence is defined by the stereochemical relation existing between the starting configuration of the reactants and the final configurations of the products.[6] Klemperer has shown[6c,6f] that the set of non-differentiable reactions in an achiral environment, *i.e.* the reaction mode according to Musher,[7] is mathematically represented by a union of double cosets of the type (1). Here

$$M^{PR}(x) = (C_P x C_R)^{PR} \cup (C_P \sigma_P x \sigma_R^{-1} C_R)^{PR} \qquad (1)$$

x represents a permutation of the group of allowed permutations S^{PR} (ref. 6) describing all the stereochemical changes possible *a priori* from the set of reactants R to the set of products P; C_R and C_P represent the appropriate configurational groups of the reactants R and products P respectively.[6e,6f] For the structures of interest in this paper, C_R and C_P are direct products of the permutational representations of the groups of symmetry operations of all the molecules constituting the reactants and products respectively; σ_R and σ_P are permutations belonging to the cosets $C_R\sigma_R$ ($= \sigma_R C_R = \sigma_R^{-1} C_R = C_R \sigma_R^{-1}$) (ref. 9) and $C_P\sigma_P$ ($=\sigma_P C_P = \sigma_P^{-1} C_P = C_P \sigma_P^{-1}$) respectively and represent inversion of configuration of *all* the ordered molecules[8] constituting the reactants and products.[6] x^{PR} and $(\sigma_P x \sigma_R^{-1})^{PR}$ represent reactions from R to P which are symmetry equivalent by an *improper* symmetry operation; in an achiral environment, such permutations represent reactions proceeding with the same rate constant, so that they are non-differentiable and belong to the same reaction mode.[6] When the set of allowed permutations S^{PR} is partitioned into sets of the type $M^{PR}(x)$,[9] a complete set of reaction modes (= set of non-differentiable reactions in an achiral environment [6]) is defined.

An elementary process having the permutational character of the mode $M^{PR}(x)$ can be represented by the operator (2) where $|M^{PR}(x)|$ represents the order of the

$$\Delta^{PR}(x) = \frac{1}{|M^{PR}(x)|} \cdot M^{PR}(x) \qquad (2)$$

set $M^{PR}(x)$; $\Delta^{PR}(x)$ is merely the set $M^{PR}(x)$ normalized to one permutation; it represents the averaged effect of all the non-differentiable permutations contained in the reaction mode $M^{PR}(x)$. These operators are particularly useful in the description of the permutational character of a reaction sequence [6] of the type (R) ⟶ (Q) ⟶ (P) where (Q) represents a short-lived intermediate. Indeed, if the reaction (R) ⟶ (Q) has the permutational character of the mode $M^{QR}(y)$ and the reaction (Q) ⟶ (P) has the permutational character of the mode $M^{PQ}(z)$, the resulting sequence of elementary processes (R) ⟶ (P) ⟶ (Q) is described by the product of operators $\Delta^{PQ}(z)\Delta^{QR}(y)$. It is shown in section 3(*a*) that this sequence can be written [6] as in (3).

$$\Delta^{PQ}(z)\Delta^{QR}(y) = \sum_x p_x^{zy} \Delta^{PR}(x) \qquad (3)$$

Relation (3) shows that the result of the application of a reaction mode $M^{QR}(y)$, followed by that of $M^{PQ}(z)$, is a linear combination of reaction modes $M^{PR}(x)$ associated with the reaction (R) ⟶ (P).[6] The coefficient p_x^{zy} represents the probability that the sequence of modes $\Delta^{PQ}(z)\Delta^{QR}(y)$ corresponds to the elementary process $\Delta^{PR}(x)$. The set of numbers in (4), where r is the

$$(z^{PQ} \longleftarrow y^{QR}) = (p_{x_1}^{zy}, p_{x_2}^{zy}, p_{x_3}^{zy}, \ldots, p_{x_r}^{zy}) \qquad (4)$$

number of reaction modes $M^{PR}(x)$, defines *the permutational character* of the sequence of the elementary processes $\Delta^{PQ}(z)\Delta^{QR}(y)$; $p_{x_i}^{zy}$ obey the relation (5).

$$\sum_{i=1}^{r} p_{x_i}^{zy} = 1 \qquad (5)$$

The calculation of these coefficients for a given intermediate (Q) is explained in section 3(*a*).

(3) *Calculation Details.*—(*a*) *Demonstration of relation* (3); *calculation of the probability coefficients.* According to relation (2) the operator $\Delta^{QR}(y)$ can be written as (6).

$$\Delta^{QR}(y) = \frac{1}{|M^{QR}(y)|} \cdot M^{QR}(y) \qquad (6)$$

$$M^{QR}(y) = (C_Q y C_R)^{QR} \cup (C_Q \sigma_Q y \sigma_R^{-1} C_R)^{QR} \qquad (7)$$

Since $M^{QR}(y)$ is a union of double cosets of the type (7), relation (6) can be rewritten as (8) [13] where the Σ's must be considered as direct sums (unions), and $c_{\alpha Q}$ and $c_{\beta R}$

$$\Delta^{QR}(y) = \frac{1}{2|C_Q||C_R|} \cdot \sum_{c_{\alpha Q}\in C_Q} \sum_{c_{\beta R}\in C_R} c_{\alpha Q}(y \cup \sigma_Q y \sigma_R^{-1}) c_{\beta R} \qquad (8)$$

range over the elements of C_Q and C_R respectively. Similarly, we can write expression (9).

$$\Delta^{PQ}(z) = \frac{1}{2|C_P||C_Q|} \cdot \sum_{c_{\gamma P}\in C_P} \sum_{c_{\delta Q}\in C_Q} c_{\gamma P}(z \cup \sigma_P z \sigma_Q^{-1}) c_{\delta Q} \qquad (9)$$

The product $\Delta^{PQ}(z)\Delta^{QR}(y)$ can be calculated from relations (8) and (9), using the rearrangement theorem for the group C_Q.[13] Relation (10) can be rewritten as (11) since expressions (12) and (13) are applicable.

$$\Delta^{PQ}(z)\Delta^{QR}(y) = \frac{1}{4|C_P||C_Q||C_R|} \cdot \sum_{c_{\alpha Q}\in C_Q} \sum_{c_{\beta R}\in C_R} \sum_{c_{\gamma P}\in C_P} [c_{\gamma P}(z \cup \sigma_P z \sigma_Q^{-1}) c_{\alpha Q}(y \cup \sigma_Q y \sigma_R^{-1}) c_{\beta R}] \qquad (10)$$

$$\Delta^{PQ}(z)\Delta^{QR}(y) = \frac{1}{4|C_P||C_Q||C_R|} \cdot \sum_{c_{\alpha Q}\in C_Q} \sum_{c_{\beta R}\in C_R} \sum_{c_{\gamma P}\in C_P} c_{\gamma P}(z c_{\alpha Q} y \cup \sigma_P z c_{\alpha Q} y \sigma_R^{-1} \cup \sigma_P z \sigma_Q^{-1} c_{\alpha Q} y \cup z c_{\alpha Q} \sigma_Q y \sigma_R^{-1}) c_{\beta R} \qquad (11)$$

$$\sum_{c_{\beta R}\in C_R} \sigma_R^{-1}(\sigma_R^{-1} c_{\beta R}) = \sum_{c_{\beta R}\in C_R} c_{\beta R} \qquad (12)$$

$$\sum_{c_{\alpha Q}\in C_Q} c_{\alpha Q}\sigma_Q = \sum_{c_{\alpha Q}\in C_Q} \sigma_Q^{-1} c_{\alpha Q} \qquad (13)$$

Relation (11) can be rewritten as (14).

$$\Delta^{PQ}(z)\Delta^{QR}(y) = \frac{1}{4|C_P||C_Q||C_R|} \cdot \sum_{c_{\alpha Q}\in C_Q} \sum_{c_{\beta R}\in C_R} \sum_{c_{\gamma P}\in C_P} c_{\gamma P}\{[z c_{\alpha Q} y \cup \sigma_P(z c_{\alpha Q} y)\sigma_R^{-1}] \cup [z c_{\alpha Q}\sigma_Q y \sigma_R^{-1} \cup \sigma_P(z c_{\alpha Q}\sigma_Q y \sigma_R^{-1})\sigma_R^{-1}]\} c_{\beta R} \qquad (14)$$

Using relation (2), similarly to (8) and (9), we obtain (15) and (16) with z, y, σ_Q, and σ_R^{-1} fixed and $c_{\alpha Q}$ ranging

$$\Delta^{PR}(x) = \frac{1}{2|C_P||C_R|} \cdot \sum_{c_{\gamma P}\in C_P} \sum_{c_{\beta R}\in C_R} c_{\gamma P}(x \cup \sigma_P x \sigma_R^{-1}) c_{\beta R} \qquad (15)$$

$$\Delta^{PQ}(z)\Delta^{QR}(y) = \frac{1}{2|C_Q|} \cdot \sum_{c_{\alpha Q}\in C_Q} [\Delta^{PR}(z c_{\alpha Q} y) + \Delta^{PR}(z c_{\alpha Q}\sigma_Q y \sigma_R^{-1})] \qquad (16)$$

over C_Q. If we define now ρ_x^{zy} and ω_x^{zy} as the number of elements $c_{\alpha Q}\in C_Q$ such that (17) and (18) are applicable

$$\Delta^{PR}(z c_{\alpha Q} y) = \Delta^{PR}(x) \qquad (17)$$

$$\Delta^{PR}(z c_{\alpha Q}\sigma_Q y \sigma_R^{-1}) = \Delta^{PR}(x) \qquad (18)$$

$$\Delta^{PQ}(z)\Delta^{QR}(y) = \sum_x \frac{\rho_x^{zy} + \omega_x^{zy}}{2|C_Q|} \cdot \Delta^{PR}(x) \qquad (19)$$

$$p_x^{zy} = (\rho_x^{zy} + \omega_x^{zy})/2|C_Q| \qquad (20)$$

respectively, then formula (16) becomes (19), *i.e.* similar to (3) if p_x^{zy} is defined as in (20). Because of the definition of ρ_x^{zy} and ω_x^{zy}, it is clear that expression (21) applies so that we obtain (22). Throughout this work,

$$\sum_x \rho_x^{zy} = \sum_x \omega_x^{zy} = |C_Q| \qquad (21)$$

$$\sum_x p_x^{zy} = 1 \qquad (22)$$

I have used relation (20) to calculate the probabilities p_x^{zy}, ρ_x^{zy} and ω_x^{zy} being obtained from relations (15)—(18).

(*b*) *Determination of the modes for the reactions* (V) ⟶ (Q) *and* (Q) ⟶ (W) (Q = X, Y, *or* Z). All the reaction modes M_j^{QV}, M_k^{WQ} (Q = X, Y, or Z), and M_t^{WV} were calculated from relation (1) and according to Klemperer's procedure.[6] The configurational groups needed for this purpose can be established from the diagrams given. These groups are [*]: (23), a group which is a

$$C_V = [I, (123),(124),(132),(134),(142),(143),(234),(243),(12)(34),(13)(24),(14)(23)] \qquad (23)$$

permutational representation of the group of proper symmetry operation of a tetrahedron (T); (24), a group

$$C_W = S_3^{123} \times S_2^{45} = [I, (123),(132),(12),(13),(23),(45),(123)(45),(132)(45),(12)(45),(13)(45),(23)(45)] \qquad (24)$$

$$C_X = [I, (132),(123),(12)(45),(13)(45),(23)(45)] \qquad (25)$$

$$C_Y = [I, (1\,234),(13)(24),(1\,432)] \qquad (26)$$

$$C_Z = I \qquad (27)$$

containing both the symmetry operations of BH_3 and H_2; and (25)—(27) which are merely the permutational representations of the proper symmetry groups of the trigonal bipyramid, the square pyramid, and the C_s intermediate, in the site labelling of X, Y, and Z respectively. In the calculation of the modes, permutations representing inversion of configuration of all the ordered molecules [8] are also needed; these are merely arbitrarily chosen improper symmetry operations. For instance, $\sigma_X = (45)$, $\sigma_Y = (13)$, $\sigma_Z = (23)(45)$, and $\sigma_V = (12)$ [see section (2)]. For the set of molecules (W), σ_W is contained in C_W because (W) is composed of a planar (BH_3) and a linear (H_2) molecule.

The set of allowed permutations associated with the reaction (V) ⟶ (W) is S_5^{WV}.[6] Representative permutations of each mode as found from relation (1) are: I^{WV} and $(15)^{WV}$ for the modes M_1^{WV} and M_2^{WV} respectively; I^{XV}, $(15)^{XV}$, $(23)^{XV}$, and $(14532)^{XV}$ for M_1^{XV}, M_2^{XV}, M_3^{XV}, and M_4^{XV}; the pairs of modes (M_1^{XV}, M_3^{XV}) [or (M_2^{XV}, M_4^{XV})] are so called enantiomeric modes [9] because, starting from a common configuration of (V), M_3^{XV} (or M_4^{XV}) generates the enantiomers of the configurations generated by M_1^{XV} (or M_2^{XV}); I^{WX}, $[(24)(35)]^{WX}$, and $(14)^{WX}$ for M_1^{WX}, M_2^{WX}, and M_3^{WX}; since the permutational representations of proper and improper symmetry operations are identical for the set of molecules (W), formula (1) reduces to (28) which is merely a double coset (7); I^{YV}, $(15)^{YV}$, and

$$M^{WX}(z) = C_W z C_X \cup C_W z \sigma_X C_X \qquad (28)$$

$$M^{WX}(z) = C_W z \Sigma_X \qquad (29)$$

$$\text{where} \qquad \Sigma_X = C_X \cup \sigma_X C_X \qquad (30)$$

$[(152)(34)]^{YV}$ for M_1^{YV}, M_2^{YV}, and M_3^{YV}, where M_2^{YV} and M_3^{YV} are enantiomeric modes; I^{WY}, $(35)^{WY}$, and $(25)^{WY}$ for M_1^{WY}, M_2^{WY}, and M_3^{WY}; I^{ZV}, $(12)^{ZV}$, $(25)^{ZV}$, $(35)^{ZV}$, and $(15)^{ZV}$ for M_1^{ZV}, M_2^{ZV}, M_3^{ZV}, M_4^{ZV}, and M_5^{ZV}; and I^{WZ}, $(24)^{WZ}$, $(14)^{WZ}$, $(25)^{WZ}$, $[(14)(25)]^{WZ}$, and $[(24)(35)]^{WZ}$ for M_1^{WZ}, M_2^{WZ}, M_3^{WZ}, M_4^{WZ}, M_5^{WZ}, and M_6^{WZ}.

(*c*) *Non-rigid intermediates.* The symmetry group of non-rigid molecules was initially defined by Longuet-Higgins.[4] Recently, Klemperer [6f] has shown that when a molecule undergoes internal motions that are rapid on the observational time scale, the proper configurational symmetry group is no longer appropriate to describe the reaction modes of a given chemical system involving that molecule. This group must be extended to a larger group containing not only all the proper symmetry operations of the molecule but also all the permutations representing the configurations that are converted into each other by the rapid internal motion under consideration; this group is called the extended configurational-symmetry group. It is a kind of Longuet-Higgins group [4] from which the operator J, representing inversion of particles about the centre of mass, has been suppressed. Let us imagine now that we want to take into account, in a reaction sequence, (R) ⟶ (Q) ⟶ (P) that the intermediate (Q) is rearranging rapidly on the time scale of the reaction (R) ⟶ (P), and that the rearrangement mode we want to consider in (Q) interconverts configurations described by the permutations contained in the group C_Q^F (F indicates ' free ' internal motion). If we want to know the permutational character of the sequence $M_k^{PQ(NR)}$-$M_j^{Q(NR)R}$, where Q(NR) indicates non-rigid (Q), we have merely to proceed as explained in section 3(*a*), except that all the elements $c_{\alpha Q}$ of C_Q must be replaced by the elements $c_{\alpha Q}^F$ of C_Q^F. The remaining procedure is the same.

For the modes of the trigonal bipyramid, the group C_X^F is either S_5 (P_1 and P_3) or A_5 (P_2 and P_4) (ref. 4*a*) containing the even permutations of S_5.[13] For the rearrangement modes of the square pyramid in which the apical ligand is moved into a basal position, $C_Y^F = S_5$. Finally, within the assumption of section 1(*d*), any rearrangement moving one or (two) ligand(s) from the H_2 subunit to the triplet leads to $C_Z^F = S_5$.

For the rearrangement modes of the C_s intermediate the following assumption was made [see section 1(*d*)]. It is admitted that the C_s intermediate rearranges rapidly ***within*** the triplet of atoms and/or the H_2 subunit.

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[*] The permutation (123) means the ligand on site 1 replaces that on site 2, the ligand on site 2 replaces that on site 3, and the ligand on site 3 replaces that on site 1, whatever the labels of these ligands may be; $(123)^{WV}$ means the ligand on site 1 in (V) replaces that on site 2 in (W), the ligand on site 2 in (V) replaces that on site 3 in (W) and the ligand on site 3 in (V) replaces that on site 1 in (W), whatever the labels of the ligands may be.

This results in an extension of the proper configurational group C_Z [relation (27)] to the group (31). This group

$$\check{C}_Z = S_3^{123} \times S_2^{45} \qquad (31)$$

and formula (1) are now used to construct the modes for (V) ⟶ (Z); under these assumptions the number of modes reduces from five to two, equations (32) and (33) in

$$\check{M}_1^{ZV} = \tilde{M}_1^{ZV} \cup \check{M}_2^{ZV} \qquad (32)$$

$$\check{M}_2^{ZV} = \check{M}_3^{ZV} \cup \tilde{M}_4^{ZV} \cup \check{M}_5^{ZV} \qquad (33)$$

which $\check{M}_1^{ZV}$ is the extended reaction mode in which H^+ does enter the H_2 subunit and $\check{M}_2^{ZV}$ is the extended mode in which H^+ does *not* enter the H_2 subunit. Using the group in formula (31) the extended permutational modes of the intermediate Z are as in (34)—(36). We

$$\check{M}_0^{Z} = \acute{C}_Z \qquad (34)$$

$$\acute{M}_1^{Z} = \grave{C}_Z(12)(45)\check{C}_Z \qquad (35)$$

$$\dot{M}_2^{Z} = \check{C}_Z(15)\check{C}_Z \qquad (36)$$

now calculate the extended configurational group associated with the modes $\tilde{M}_1^{Z}$ and $\hat{M}_2^{Z}$ (see refs. 4*a* and 4*h*). This gives $C_Z^{F} = S_5$, so that, as for the non-rigid trigonal bipyramid and square pyramid, the resulting permutational character of the reaction sequence (V) ⟶ $(Z)^{NR}$ ⟶ (W) is $\left(\frac{2}{5}, \frac{3}{5}\right)_{Z(NR)}^{WV}$.

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