dissociative Eigen mechanism for reactions of divalent transition metal ions such as nickel(II) and cobalt(II) has recently received support by the observation[21] that their substitution reactions with some uncharged ligands are characterized by markedly positive ΔV^*.

It should be noted that the value of ΔH^* for aquo exchange with $Rh(NH_3)_5OH_2^{3+}$ is actually 2.0 kcal mol^{-1} *less* than for the analogous reaction of $Co(NH_3)_5OH_2^{3+}$, whereas for any probable geometry of the transition states the ligand field contribution to ΔH^* should be at least 20 kcal mol^{-1} *greater* for Rh(III) than for Co(III).[22] This indicates that ligand field effects cannot be a major component of ΔH^* in substitution reactions at *both* Rh(III) and Co(III) centers. Our assignment of an associative mechanism for Rh(III) and a dissociative one for Co(III) provides an explanation for this observation, since the energy of bond formation between the incoming aqua nucleophile and the Rh(III) center could lower the activation enthalpy to a value less than that of the Co(III) substitution. The increased importance of the associative mechanism as one descends a periodic group can be attributed to the enhanced tendency of the larger central metal atom to engage in covalent bonding to the incoming nucleophile (as measured by the "Class B" character[23] or "softness"[24] of the metal atom), and to the reduced steric hindrance to the entry of the seventh ligand.

The factors favoring an associative mechanism for Cr(III) as opposed to a dissociative mechanism for Co(III) remain unresolved. Calculations of the ligand field contributions to ΔH^*, made by Spees, Perumareddi and Adamson[22] on the basis of assumed spin pairing in the transition state, do indeed suggest that a seven-coordinate transition state of local D_{5h} symmetry may be favored over alternative dissociative pathways for Cr(III), while a five-coordinate transition state may be favored, albeit marginally, for analogous Co(III) systems. However, the general observation[25] that stereochemical change is rarely encountered in Cr(III) substitutions is difficult to reconcile with a transition state of D_{5h} symmetry, and the Spees–Perumareddi–Adamson calculations indicate that the most likely alternative stereoretentive seven-coordinate transition state, which would have C_{2v} local symmetry, would involve a higher ligand-field contribution to ΔH^*. A further uncertainty arising from the Spees–Perumareddi–Adamson analysis is that the alternative assumption of a high-spin transition state for substitutions at Cr(III) leads to the result that ligand-field effects would favor a dissociative process.

We conclude that the analysis of ΔH^* values in terms of ligand-field effects, as in the Spees–Perumareddi–Adamson approach, involves significant uncertainties when applied to the problem of reaction mechanisms. While considerations of ΔS^* values are rather more definitive, in the case of the aquo exchanges there still remains the ambiguity from the unknown molecularity with respect to the solvent as a nucleophile. This uncertainty can involve even the sign of ΔS^* as well as its numerical magnitude. By contrast, the sign and values of ΔV^* appear to be more reliable in establishing reaction mechanisms for aquo exchange systems such as those described in this paper.

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[22] S. T. Spees, J. R. Perumareddi, and A. W. Adamson, *J. Amer. Chem. Soc*, 90, 6626 (1968).

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Dynamic Stereochemistry of Polytopal Isomerization Reactions

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Abstract: Following the approach taken in studies of permutational isomerization reactions, polytopal isomerization reactions are defined in terms of permutation operations. The point group symmetry of the interconverting polytopal isomers is used to generate classes of symmetry equivalent reactions. Formulas for enumerating these classes are provided. Topological representations are then defined in a precise fashion and various properties are examined. The relationship between a polytopal isomerization reaction and the permutational isomerization reactions it implies is also discussed. Finally, some nonrigid inorganic, organic, and organometallic molecules are treated to show the usefulness of these formalisms.

The ligands or substituents of many molecules define polytopes, *i.e.*, polygons or polyhedra. Within this class of molecules, isomers defining different polytopes are designated polytopal isomers.[2] The concept of polytopal isomerism has proven to be useful in unifying seemingly diverse areas of structural chemistry. While the structural stereochemistry of poly-

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[1] National Science Foundation Predoctoral Fellow.

[2] As originally defined,[3] polytopal isomers are characterized by their idealized polytopal forms in order to maximize symmetry. In this paper, the "nonidealized" shape of polytopal isomers will be considered and the symmetry of each polytopal form will be the standard molecular point group symmetry.

[3] E. L. Muetterties, *J. Amer. Chem. Soc.*, 91, 1636 (1969).

topal isomers can be discussed in terms of well-defined geometric and topological concepts,[4] the need for a systematic and comprehensive treatment of the dynamic stereochemistry has been recognized.[5] This paper represents an attempt to provide an approach which is meaningful and useful in a physical as well as mathematical sense. While the use of models has usually obviated formal permutational approaches to structural stereochemistry, the representational difficulties encountered in dynamic stereochemistry necessitate a formal approach.

In this paper, an isomerization process will be characterized by the stereochemical relation of the reactant isomer and the product isomer. We thus speak of isomerization reactions as opposed to isomerization mechanisms. Different isomerization mechanisms may of course imply the same isomerization reaction, but by experimentally establishing an isomerization reaction, certain postulated mechanisms may be ruled out. Characterization of an isomerization reaction is therefore the first step toward verification of a proposed mechanism.

To simplify discussion, only systems of two interconverting polytopal isomers will be discussed in this paper. Also, only molecules having ligands of two different chemical identities will be considered. All the concepts presented may be easily extended to cover more general cases.

When a given polytopal isomerization reaction interconverts two polytopal isomers, the assumption is always made here that any intermediate configuration has a connectivity[3] equal to two. Thus the reactions considered here may be unequivocally defined in terms of one reactant isomer and one product isomer.

Definitions and Nomenclature

Let $\bar{R}$ and $\bar{T}$ be the point groups of two polytopal isomers. Let the groups R and T consist of all proper rotation operations in $\bar{R}$ and $\bar{T}$, respectively. The symbols R and T will also be used as labels which identify the geometries of the two polytopal forms.

The set of n (unidentate) ligands is assigned indexed labels $L_l \equiv \{l_1, l_2, \ldots, l_n\}$ so that all ligands are distinguishable. The n skeletal positions of polytopal isomers R and T are assigned indexed labels $\chi_s^R \equiv \{s_1^R, s_2^R, \ldots, s_n^R\}$ and $\chi_s^T \equiv \{s_1^T, s_2^T, \ldots, s_n^T\}$, respectively. Permutational isomers of polytopal isomer R are described by $2 \times n$ matrices

$$\begin{pmatrix} l \\ s \end{pmatrix}^R = \begin{pmatrix} 123\ldots n \\ ijk\ldots l \end{pmatrix}^R$$

where ligand indices are listed in the top row and below each ligand index is written the index of the skeletal position which that ligand occupies. $\binom{l}{s}^T$ is defined similarly.

$$\begin{pmatrix} l \\ s \end{pmatrix}_e^R \equiv \begin{pmatrix} 123\ldots n \\ 123\ldots n \end{pmatrix}^R \text{ and } \begin{pmatrix} l \\ s \end{pmatrix}_e^T \equiv \begin{pmatrix} 123\ldots n \\ 123\ldots n \end{pmatrix}^T$$

are called *reference isomers*. The isomers drawn in Figure 1 illustrate this nomenclature.

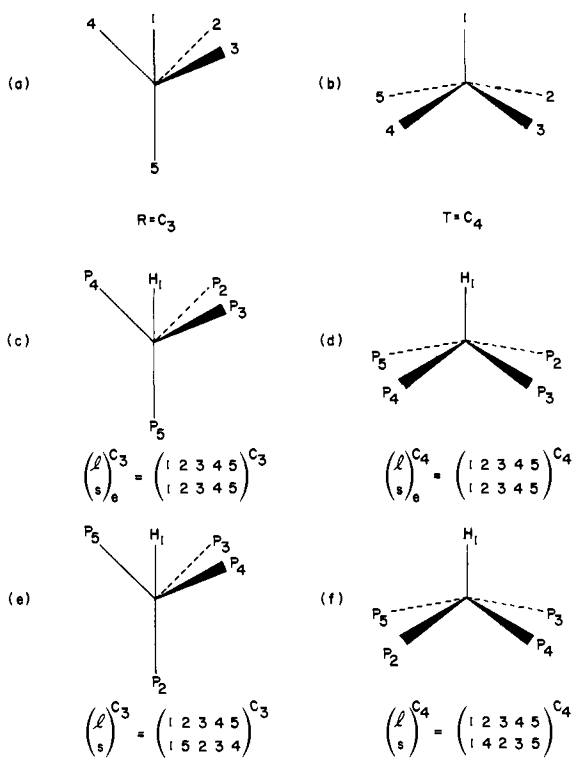

Figure 1. Some polytopal and permutational isomers of the molecule MHP_4. H might represent a hydride ligand and P a trisubstituted phosphorus ligand. (a) and (b) indicate the indexing of skeletal positions. (c)–(f) show some isomers and the appropriate $\binom{l}{s}$ matrices.

Assume that the set of n ligands contains n_1 ligands of one chemical identity (type I) and n_2 ligands of a different chemical identity (type II). Ligands of type I are labeled with $l_1, l_2, \ldots, l_{n_1}$ and ligands of type II are labeled with $l_{n_1+1}, l_{n_1+2}, \ldots, l_n$. Also, skeletal positions with indices $1, 2, \ldots, n_1$ are occupied by ligands of type I, and skeletal positions with indices $n_1 + 1$, $n_1 + 2$, $\ldots$, n are occupied by ligands of type II. We define a group H, the *group of allowed permutations*, which acts on the numbers $1, 2, \ldots, n$ and contains all permutations which permute the numbers $1, 2, \ldots, n_1$ among themselves and the numbers $n_1 + 1$, $n_1 + 2$, $\ldots$, n among themselves. H therefore contains $n_1! \cdot n_2!$ permutations. Formally, $H = S_{n_1} + S_{n_2}$, the direct sum[6] of the symmetric groups S_{n_1} and S_{n_2}.

As shown previously,[7] representations of the group of allowed permutations are used to describe permutational isomerization reactions. Letting H map χ_s^R onto χ_s^R by operating on the indices of the skeletal positions, a representation H^{RR} is formed. Each $h_i^{RR} \in H^{RR}$ is a permutation operation which describes a permutational isomerization reaction and/or a point group operation of the polytopal isomer R. H^{RR} is a group with the product operation defined by

$$h_i^{RR} \cdot h_j^{RR} = (h_i \cdot h_j)^{RR}$$

Products are read from right to left throughout this paper. The operations of the point group R can be represented by the permutation group R^{RR} which operates on the indices of the skeletal positions of polytopal

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(4) E. L. Muetterties and C. M. Wright, *Quart. Rev. Chem. Soc.*, **21**, 109 (1967).

(5) G. Binsch, E. L. Eliel, and H. Kessler, *Angew. Chem.*, **83**, 618 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 570 (1971).

(6) For a rigorous definition see R. W. Robinson, *J. Combinatorial Theory*, **4**, 184 (1968), or F. Harary, "Graph Theory," Addison-Wesley, Reading, Mass., 1969, p 163.

(7) W. G. Klemperer, *Inorg. Chem.*, **11**, 2668 (1972).

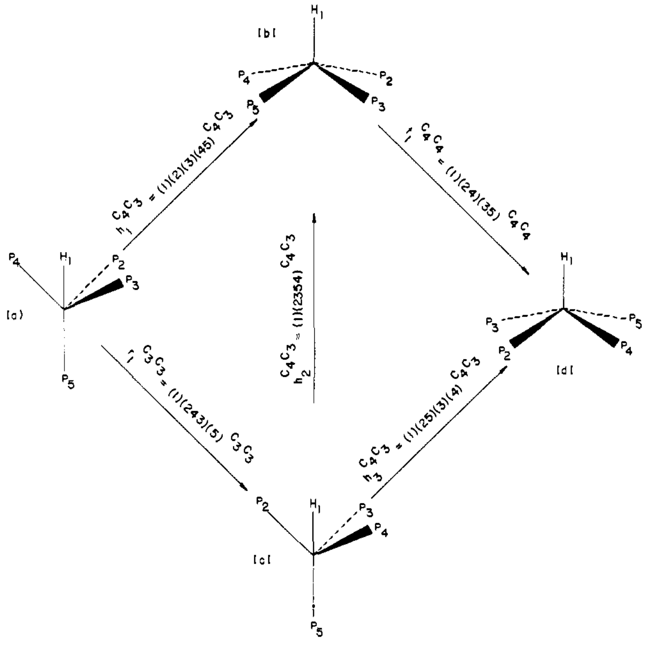

Figure 2. A scheme which illustrates the relationship between three reactions $h_1^{C_4C_3}$, $h_2^{C_4C_3}$, and $h_3^{C_4C_3}$ which are all nondifferentiable in a chiral environment. Skeletal positions are indexed as in Figure 1.

isomer R. $\bar{R}^{RR}$ similarly represents the point group $\bar{R}$. Letting H map χ_s^T onto χ_s^T by operating on the indices of the skeletal positions, the group H^{TT} is defined. Subgroups T^{TT} and $\bar{T}^{TT}$ represent the point groups T and $\bar{T}$, respectively.

Although products of the type $h_i^{TT}\cdot h_j^{RR}$ are undefined, operations such as $r_i^{TT} \epsilon R^{TT}$ have meaning. Let R be a subgroup of H such that the representation R^{RR} is generated when R maps χ_s^R onto χ_s^R by operating on the indices of the skeletal positions. Although the same symbol is used for point group and its permutation group representation, the intended meaning should be clear from context. The representation R^{TT} is formed when R maps χ_s^T onto χ_s^T by operating on the indices of the skeletal positions. The permutation groups $\bar{R}$, T, and $\bar{T}$ are defined in the same fashion so that $\bar{R}^{TT}$, T^{RR}, and $\bar{T}^{RR}$ are well-defined groups. In Figure 1, we let $R = C_3$. Then $r_i^{C_3C_3} = (1)(234)(5)^{C_3C_3}$ represents a rotation of the C_3 polytopal isomer. $r_i^{C_4C_4} = (1)(234)(5)^{C_4C_4}$, however, describes a permutation isomerization reaction of the C_4 isomer which converts isomer f into isomer d.

The group of allowed permutations can also be used to describe polytopal isomerization reactions. Letting each $h_i \epsilon H$ represent a mapping of χ_s^R onto χ_s^T by operating on the indices of the skeletal positions, we form a pseudo-representation[8] of H, H^{TR}. Any polytopal isomerization reaction which converts isomers having geometry R into isomers having geometry T can be described by an $h_i^{TR} \epsilon H^{TR}$. For example, $h_i^{C_4C_3} = (1)(2)(3)(45)^{C_4C_3}$ is a polytopal isomerization which converts isomer e in Figure 1 into isomer f; *i.e.*, the permutation (1)(2)(3)(45) acts on the bottom row of

$$\begin{pmatrix} 12345 \\ 15234 \end{pmatrix}^{C_3}$$

giving the bottom row of

$$\begin{pmatrix} 12345 \\ 14235 \end{pmatrix}^{C_4}$$

In chemical terms, the operation $(1)(2)(3)(45)^{C_4C_3}$ means "the ligand in skeletal position $s_1^{C_3}$ is moved to skeletal position $s_1^{C_4}$, the ligand in position $s_2^{C_3}$ is moved to position $s_2^{C_4}$, the ligand in position $s_3^{C_3}$ is moved to position $s_3^{C_4}$, the ligand in position $s_4^{C_3}$ is moved to position $s_5^{C_4}$, and the ligand in position $s_5^{C_3}$ is moved to position $s_4^{C_4}$." H^{RT} and H^{TR} are not groups since products of the type $h_i^{RT}\cdot h_j^{RT}$ are undefined. However, products

$$h_i^{RT}\cdot h_j^{TR} = (h_i\cdot h_j)^{RR}$$

and

$$h_i^{RT}\cdot h^{TT} = (h_i\cdot h_j)^{RT}$$

are well defined. The reverse reaction of the polytopal isomerization reaction h_j^{TR} is defined by

$$(h_j^{TR})^{-1} \equiv (h_j^{-1})^{RT}$$

The principle of microscopic reversibility[9] guarantees that the definition is physically meaningful.

Although the definitions and nomenclature presented in this section have been made with reference to polytopal isomers, it should be clear to the reader that they are equally valid for the description of stereoisomerization reactions of any symmetric molecules.

Enumeration Procedures

Since the set H^{TR} contains $n_1!n_2!$ operations, one might conclude that there exist $n_1!n_2!$ distinct polytopal isomerization reactions which convert polytopal isomers having geometry R into isomers having geometry T. This would indeed be the case if both isomers were fixed in an asymmetric environment. In most experimental situations, however, the isomers are free to rotate in a symmetric environment, and therefore certain polytopal isomerization reactions in H^{TR} become symmetry equivalent. See, for example, the reactions shown in Figure 2. Reaction $h_1^{C_4C_3}$ converts isomer a to isomer b. Since isomers are assumed to be free to rotate in space, a and c are indistinguishable and the reaction which converts a into b will be nondifferentiable from the reaction which converts c into b because reactions are defined solely in terms of reactant and product isomers. Mathematically speaking, $h_1^{C_4C_3}$ and $h_2^{C_4C_3}$ are symmetry equivalent because

$$h_1^{C_4C_3} = h_2^{C_4C_3}\cdot r_1^{C_3C_3} \equiv (h_2\cdot r_1)^{C_4C_3}$$

i.e., $h_1 = h_2\cdot r_1$, $r_1 \epsilon C_3$. Using the same arguments on the symmetry of the product isomer, $h_3^{C_4C_3}$ and $h_2^{C_4C_3}$ are symmetry equivalent because $h_3 = t_1\cdot h_2$, $t_1 \epsilon C_4$. Also, $h_1^{C_4C_3}$ and $h_3^{C_4C_3}$ are equivalent since $h_3 = t_1\cdot h_1\cdot r_1^{-1}$. We therefore make the following definitions.

Two polytopal isomerization reactions h_i^{TR} and h_j^{TR} are *nondifferentiable polytopal isomerization reactions* in a chiral environment if eq 1 holds for some permutation $r_i \epsilon R$ and some permutation $t_j \epsilon T$.

$$h_i = t_j\cdot h_j\cdot r_i \qquad (1)$$

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(8) H^{TR} is not a true representation, since H^{TR} is not a group (*vide infra*).

(9) For further discussion, see R. L. Burwell, Jr., and R. G. Pearson, *J. Phys. Chem.*, 70, 300 (1966).

h_i^{TR} and h_j^{TR} are *differentiable polytopal isomerization reactions* in a chiral environment if eq 1 does not hold.

The relation between h_i and h_j defined in eq 1 is an equivalence relation which may be used to partition H into sets of equivalent operations called double cosets Th_iR.[10] These double cosets can be enumerated using eq A1 given in Appendix I. D_{TR} is the number of double cosets Th_iR in H. Consequently, the set H^{TR} can be partitioned into D_{TR} different sets containing nondifferentiable reactions. We say that D_{TR} is the number of polytopal isomerization reactions differentiable in a chiral environment. As shown in Appendix I, $D_{TR} = D_{RT}$.

Many experimental techniques are unable to distinguish enantiomeric isomers. Using the same arguments given at the beginning of this section, one finds that this indistinguishability renders two polytopal isomerization reactions h_i^{TR} and h_j^{TR} symmetry equivalent if

$$h_i^{TR} = \bar{t}_k^{TT} \cdot h_j^{TR} \cdot \bar{r}_l^{RR}$$

for some $\bar{t}_k^{TT} \in \bar{T}^{TT}$ and some $\bar{r}_l^{RR} \in \bar{R}^{RR}$. Accordingly, we define h_i^{TR} and h_j^{TR} to be nondifferentiable polytopal isomerization reactions in a totally symmetric environment if eq 2 holds for some $\bar{r}_i \in \bar{R}$ and some $\bar{t}_j \in \bar{T}$.

$$h_i = \bar{t}_j \cdot h_j \cdot \bar{r}_i \tag{2}$$

h_i^{TR} and h_j^{TR} are differentiable in a totally symmetric environment if eq 2 does not hold. $D_{\bar{T}\bar{R}} = D_{\bar{R}\bar{T}}$, defined as the number of reactions differentiable in a totally symmetric environment, is calculated using eq A1 given in Appendix I.

Topological Representation

Assume that a polytopal isomerization reaction h_o^{TR} and consequently its reverse reaction $(h_o^{-1})^{RT}$ interconvert polytopal isomers R and T. The interconversions may be clearly viewed by constructing a topological representation.[3] The topological representation of a polytopal isomerization reaction is a graph defined by labeled points representing permutational isomers of both polytopal isomers and lines which represent polytopal isomerization reactions. Two points are connected by a line if the reactions h_o^{TR} and $(h_o^{-1})^{RT}$ interconvert the isomers which these points represent. In this section, the definitions given above will be used to define the structure of a topological represenation and then show which reactions must generate identical topological representations. Then the concept of connectivity[3] will be discussed. Many procedures followed in this section have been outlined rigorously elsewhere[11] and will not be repeated here in detail.

The set of $n_1!n_2!$ matrices $\binom{l}{s}^R$ generated when H^{RR} acts on the reference isomer $\binom{l}{s}_e^R$ contains all permutational isomers of polytopal form R. Two matrices $\binom{l}{s}_i^R$ and $\binom{l}{s}_j^R$ represent the same permutational isomer if $\binom{l}{s}_j^R = r_k^{RR}\binom{l}{s}_j^R$, $r_k \in R$. Therefore, if we partition H^{RR} into right cosets $R^{RR} \cdot h_l^{RR}$, each coset represents a permutational isomer. Since there exist $|H^{RR}|/|R| = n_1!n_2!/|R|$ cosets, where $|R|$ is the number of operations in R, there exist $n_1!n_2!/|R|$ permutational isomers of polytopal isomer R. We choose one element from each coset and

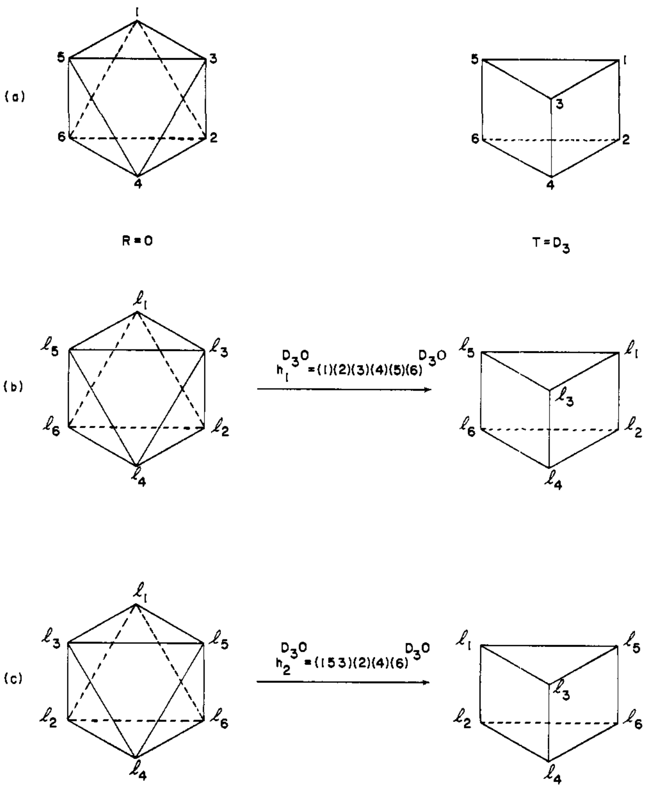

Figure 3. Two enantiomeric polytopal isomerization reactions. (a) defines the indexing of skeletal positions. (b) and (c) show the reactions.

combine these elements to form a set C^R, the set of coset representatives. Each $c_i^R \in C^R$ represents a unique permutational isomer.

$$I_R \equiv |C^R| = n_1!n_2!/|R|$$

is called the isomer count[3] of polytopal isomer R.

$$I_T \equiv |C^T| = n_1!n_2!/|T|$$

is defined similarly. Elements in the sets C^R and C^T are used to label the points of a topological representation. A line will connect points c_i^R and c_j^T if

$$t_k^{TT} \cdot c_j^T = h_o^{TR} \cdot r_l^{RR} \cdot c_i^R \tag{3}$$

i.e., $c_j^T = (t_k^{-1} \cdot h_o r_l)^{TR} \cdot c_i^R$ for some $r_l \in R$ and $t_k \in T$. Arguments used in ref 11 may be applied to show that two polytopal isomerization reactions h_i^{TR} and h_j^{TR} will generate identical topological representations if h_i^{TR} and h_j^{TR} are formally nondifferentiable in a chiral environment.

If polytopal isomerization reactions occur in an achiral environment,[12] certain reactions which are formally differentiable in a chiral environment will always be experimentally nondifferentiable and therefore should be defined as generating the same topological representation. For example, the reactions $h_1^{D_3O}$ and $h_2^{D_3O}$ shown in Figure 3 are formally differentiable in a chiral environment. In an achiral environment, however, they have equal probabilities of occurring since they differ only in that one reaction describes a net counter-

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(10) M. Hall, Jr., "The Theory of Groups," Macmillan, New York, N. Y., 1959, pp 14–15.

(11) W. G. Klemperer, *J. Amer. Chem. Soc.*, **94**, 6940 (1972).

(12) An achiral environment is an environment which has reflection symmetry as opposed to a chiral environment, which does not have reflection symmetry. In the present case where molecules are free to rotate in solution or the gas phase, it is of course assumed that the environment has complete rotational symmetry.

clockwise rotation of an octahedral face, while the other describes a net counterclockwise rotation of an octahedral face. We shall define this "chirality phenomenon" precisely.

If $R \neq \bar{R}$ and $T \neq \bar{T}$,[13] then $\binom{l}{s}_u^R$ and $\bar{r}_o^{RR}\binom{l}{s}_u^R$ as well as $\binom{l}{s}_v^T$ and $\bar{t}_o^{TT}\binom{l}{s}_v^T$ represent enantiomers if $\bar{r}_o^{RR}$ and $\bar{t}_o^{TT}$ represent improper operations in $\bar{R}$ and $\bar{T}$, respectively. If

$$h_o^{TR}\begin{pmatrix} l \\ s \end{pmatrix}_u^R = \begin{pmatrix} l \\ s \end{pmatrix}_v^T$$

then the reaction h_p^{TR} which converts $\bar{r}_o^{RR}\binom{l}{s}_u^R$ into $\bar{t}_o^{TT}\binom{l}{s}_v^T$ must occur with equal probability in an achiral environment. Since

$$h_p^{TR} \cdot \bar{r}_o^{RR}\begin{pmatrix} l \\ s \end{pmatrix}_u^R = \bar{t}_o^{TT}\begin{pmatrix} l \\ s \end{pmatrix}_v^T$$

it follows that

$$(\bar{t}_o^{-1} \cdot h_p \cdot \bar{r}_o)^{TR}\begin{pmatrix} l \\ s \end{pmatrix}_u^R = \begin{pmatrix} l \\ s \end{pmatrix}_v^T$$

and therefore

$$h_o = \bar{t}_o^{-1} \cdot h_p \cdot \bar{r}_o$$

This relation motivates the following definitions.

Two polytopal isomerization reactions h_i^{TR} and h_j^{TR} are "mirror images" if

$$h_i = \bar{t}_k \cdot h_j \cdot \bar{r}_l$$

where $\bar{t}_k$ and $\bar{r}_l$ are operations in $\bar{T}$ and $\bar{R}$, respectively, which represent improper point group operations. If h_i^{TR} and h_j^{TR} are also formally differentiable in a chiral environment, then they are *enantiomeric reactions*, or simply *enantiomers*. Either reaction may be referred to as a *chiral reaction*. If a reaction and its "mirror images" are nondifferentiable in a chiral environment, we call the reaction an *achiral reaction*.

As a result of this digression, we note that two reactions h_o^{TR} and h_p^{TR} should generate the same topological representation if they are enantiomeric reactions. Accordingly, for the case of a chiral reaction h_o^{TR}, two points c_i^R and c_j^T are connected by a line if and only if eq 3 or eq 4 holds for some $r_l \in R$, $t_k \in T$, and h_p^{TR}, an enantiomer of h_o^{TR}.

$$t_k^{TT} \cdot c_j^T = h_p^{TR} \cdot r_l^{RR} \cdot c_i^R \tag{4}$$

When the polytopal isomerization reaction h_o^{TR} and its "mirror image" h_p^{TR} operate on the permutational isomer represented by c_i^R, the number of different permutational isomers of polytopal isomer T which may result is defined as the *connectivity* δ_R. δ_T is defined similarly. In terms of a topological representation, δ_R is the number of different points c_j^T which are connected to any given c_i^R by a single line, and δ_T is the number of different points c_i^R which are connected to any given c_j^T by a single line. The value of δ_R and δ_T is invariant with respect to choice of c_i^R and c_j^T, as shown in Appendix II.

Connectivities can be calculated using formulas presented in Appendix II. If h_o^{TR} is an achiral reaction, then δ_R and δ_T are evaluated using eq 5 and 6.

$$\delta_R = \frac{|R|}{|R \cap h_o^{-1}Th_o|} \tag{5}$$

$$\delta_T = \frac{|T|}{|T \cap h_oRh_o^{-1}|} \tag{6}$$

Here, $|R|$ and $|T|$ are the number of operations in the groups R and T, respectively. $|R \cap h_o^{-1}Th_o|$ is the number of operations which the groups R and $h_o^{-1}Th_o$ have in common. Similarly, $|T \cap h_oRh_o^{-1}|$ is the number of operations which the groups T and $h_oRh_o^{-1}$ have in common. If h_o^{TR} is chiral, then eq 7 and 8 are used to calculate connectivities.

$$\delta_R = \frac{2|R|}{|R \cap h_o^{-1}Th_o|} \tag{7}$$

$$\delta_T = \frac{2|T|}{|T \cap h_oTh_o^{-1}|} \tag{8}$$

Equations 5–8 simplify when $h_o = e$, the identity operation. This is the case for the first reaction shown in Figure 3. Since the labeling of skeletal positions is arbitrary, skeletal positions may always be indexed such that any one specific polytopal isomerization reaction is represented by the identity operation.

By labeling skeletal positions such that $h_o^{TR} = e^{TR}$, eq 5 and 6 (or eq 7 and 8) may be combined to show that

$$\delta_R/\delta_T = |R|/|T|$$

Since $I_R = n_1!n_2!/|R|$ and $I_T = n_1!n_2!/|T|$

$$I_T/I_R = |R|/|T|$$

Consequently

$$I_T\delta_T = I_R\delta_R \tag{9}$$

Since no assumptions were made regarding closure properties,[3] this relation must hold for both closed and open systems. Of course it is assumed that the polytopal isomerization process under discussion may be characterized by one permutation operation, h_o^{TR}. This will always be true if only one polytopal isomerization mechanism is operative and all intermediate configurations have connectivities equal to two. Also, the physical validity of eq 5–8 is based on the assumption that for polytopal isomers R and T, "memory effects" are ruled out (*vide infra*).

Permutational Isomerization *via* Intermediate Polytopal Configurations

In previous papers dealing with permutational isomerization reactions, a particular rearrangement process could be characterized by a single permutation operation since the assumption was made that all intermediate configurations[14] had connectivities of two. When a permutational isomerization process proceeds *via* an intermediate configuration having a connectivity greater than two, it may be necessary to use two or more differentiable permutational isomerization reactions to describe the process.

Let polytopal isomers having geometry R undergo permutational isomerization *via* the intermediate poly-

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[13] This assumption is equivalent to the assumption that the polytopal isomers have nonplanar achiral skeletal frameworks as well as achiral ligands. Other cases can be treated, but the problem becomes more complex.

[14] By "intermediate configurations" is meant any configuration assumed by a molecule during the course of an isomerization reaction. It need not correspond to a metastable intermediate or a transition state; *i.e.*, it may characterize any point on the potential energy surface defined by the reaction pathway.

topal configuration T. Also, let the polytopal isomerization reaction h_o^{TR} characterize this process. We first assume that h_o^{TR} is achiral. Then all implied permutational isomerization reactions of isomers having geometry R have the form

$$r_k^{RR} \cdot (h_o^{-1})^{RT} \cdot t_i^{TT} \cdot h_o^{TR} \cdot r_i^{RR} = (r_k \cdot h_o^{-1} \cdot t_i \cdot h_o \cdot r_i)^{RR}$$

where r_i, $r_k \in R$, $t_i \in T$. Since we are at this point only interested in permutational isomerization reactions differentiable in a chiral environment,[7] only the set of $|T|$ operations

$$(h_o^{-1}Th_o)^{RR} \equiv (h_o^{-1} \cdot t_i \cdot h_o)^{RR},\ t_i \in T$$

is of interest. This set is called the set of permutational isomerization reactions implied by h_o^{TR}. If h_o^{TR} is chiral and h_p^{TR} is an enantiomeric reaction, then the $4|T|$ operations $(h_p^{-1}Th_p)^{RR}$, $(h_p^{-1}Th_o)^{RR}$, $(h_o^{-1}Th_p)^{RR}$, and $(h_o^{-1}Th_o)^{RR}$ define the set of permutational isomerization reactions implied by h_o^{TR}. In either case, this set may be partitioned into $x + 1$ subsets such that one subset contains a_o operations in R and each of the remaining x subsets is a maximal subset of reactions nondifferentiable in a chiral environment. Then

$$\psi^{RR}(h_o^{TR}) \equiv a_oe + a_1h_1 + a_2h_2 + \cdots + a_xh_x$$

defines a set of x permutational isomerization reactions differentiable in a chiral environment. The reaction h_i^{RR} corresponding to each h_i in this expression is nondifferentiable from the reactions in the ith subset in a chiral environment, and a_i is the number of reactions in the ith subset. If the intermediate polytopal configuration T describes a metastable intermediate, then $a_i/\Sigma^x{}_{i=1}a_i$ is the probability that a permutational isomerization reaction nondifferentiable from h_i in a chiral environment will occur each time isomer R undergoes permutational isomerization *via* the intermediate T. If the intermediate polytopal configuration T does not describe a metastable intermediate, then $a_i/\Sigma^x{}_{i=1}a_i$ may or may not have physical significance. If it does not, we say that "memory effects" are operative.

For the interpretation of spectroscopic studies

$$\bar{\psi}^{RR}(h_o^{TR}) \equiv b_oe + b_1h_1 + b_2h_2 + \cdots + b_yh_y$$

may be of interest. This expression defines a set of permutational isomerization reactions which are differentiable in a totally symmetric environment. $\bar{\psi}^{RR}(h_o^{TR})$ is obtained by partitioning the set of permutational isomerization reactions implied by h_o^{TR} into $y + 1$ subsets such that one subset contains b_o operations in R and each of the other y subsets is a maximal subset of reactions nondifferentiable in a totally symmetric environment. h_i^{RR} is nondifferentiable from the reactions in the ith subset in a totally symmetric environment, and the ith subset contains b_i operations.

Examples

In this section, four examples will be treated which illustrate the usefulness of the above definitions and formulas in solving stereochemical problems. The first example shows how polytopal isomerization reactions are enumerated. Next, the procedure for calculating connectivities is demonstrated. Then a system is discussed which undergoes permutational isomerization *via* an intermediate polytopal configuration. The last example indicates how more complex systems may be treated.

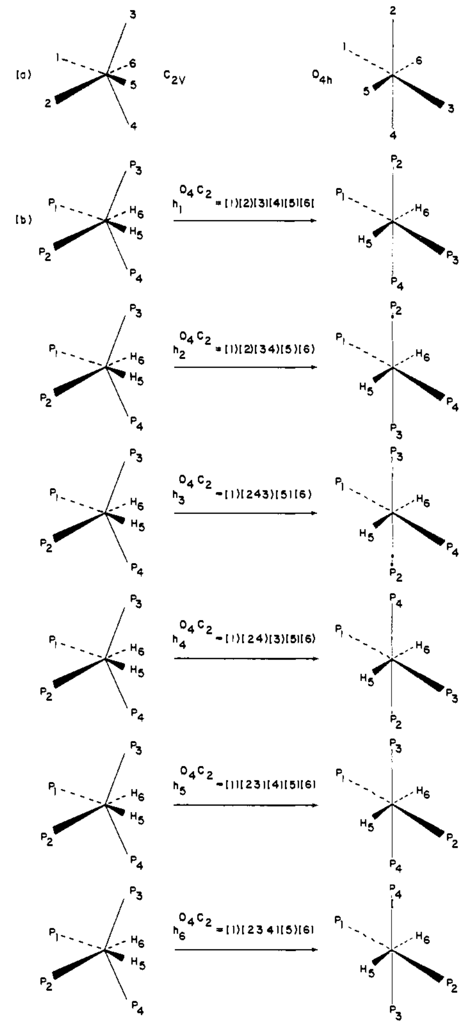

Figure 4. Six polytopal isomerization reactions are shown in (b). Indexing of skeletal positions is defined in (a).

Cis–Trans Isomerization of MH_2P_4. The stereochemistry of molecules MH_2P_4, where M = Fe, Ru, Os, H = a hydride ligand, and P = a trisubstituted phosphorus ligand, has been studied in detail.[15] Certain molecules of this type exist in both cis and trans forms, and these two polytopal isomers interconvert in solutions. We shall now examine all the distinct polytopal isomerization reactions which might describe the stereochemical change involved.

The skeletal positions of the two polytopal forms are labeled as shown in Figure 4a. $n_1 = 4$, $n_2 = 2$, and the set of ligands is assigned the labels $\{P_1, P_2, P_3, P_4, H_5, H_6\}$. Also, $\bar{R} = C_{2v}$, $R = C_2$, $\bar{T} = D_{4h}$, and $T = D_4$. The generalized cyclic type of each operation in the permutation groups generated by these point groups is shown in Table I. With this information in hand, we first calculate $D_{D_4C_2}$, the number of polytopal isomerization reactions differentiable in a chiral environment. Letting $B = D_4$ and $W = C_2$ in eq A1

$$D_{D_4C_2} = \frac{1}{|D_4||C_2|}\sum_{D_4,\,C_2}(h^{D_4}{}_{j_1j_2j_3j_4.k_1k_2})(h^{C_2}{}_{j_1j_2j_3j_4.k_1k_2}) \times \prod_{i=1}^{4}(j_i!i^{j_i})\prod_{l=1}^{2}(k_l!l^{k_l}) \quad (10)$$

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(15) J. P. Jesson in "Transition Metal Hydrides," E. L. Muetterties, Ed., Marcel Dekker, New York, N. Y., 1971, pp 180–189.

Table I. Permutation Group Operations Generated When C_{2v} and D_{4h} Act on the Indices of Skeletal Positions Defined in Figure 4a[a]

Group	Point group operations	Permutation group operations	Generalized cyclic type
	E	$r_1 = \bar{r}_1 = (1)(2)(3)(4)(5)(6)$	(4,0,0,0;2,0)
$R = C_2$	C_2	$r_2 = \bar{r}_2 = (12)(34)(56)$	(0,2,0,0;0,1)
$\bar{R} = C_{2v}$	σ_v	$\bar{r}_3 = (1)(2)(34)(5)(6)$	(2,1,0,0;2,0)
	σ_v'	$\bar{r}_4 = (12)(3)(4)(56)$	(2,1,0,0;0,1)
	E	$t_1 = \bar{t}_1 = (1)(2)(3)(4)(5)(6)$	(4,0,0,0;2,0)
	C_4	$t_2 = \bar{t}_2 = (1234)(5)(6)$	(0,0,0,1;2,0)
	C_4^{-1}	$t_3 = \bar{t}_3 = (1432)(5)(6)$	(0,0,0,1;2,0)
	C_4^2	$t_4 = \bar{t}_4 = (13)(24)(5)(6)$	(0,2,0,0;2,0)
	C_2	$t_5 = \bar{t}_5 = (1)(24)(3)(56)$	(2,1,0,0;0,1)
	C_2	$t_6 = \bar{t}_6 = (13)(2)(4)(56)$	(2 1,0,0;0,1)
	C_2'	$t_7 = \bar{t}_7 = (12)(34)(56)$	(0,2,0,0;0.1)
$T = D_4$	C_2'	$t_8 = \bar{t}_8 = (14)(23)(56)$	(0,2,0,0;0,1)
$\bar{T} = D_{4h}$	i	$\bar{t}_9 = (13)(24)(56)$	(0,2,0,0;0,1)
	S_4	$\bar{t}_{10} = (1234)(56)$	(0,0,0,1;0,1)
	S_4^{-1}	$\bar{t}_{11} = (1432)(56)$	(0,0,0,1;0,1)
	σ_h	$\bar{t}_{12} = (1)(2)(3)(4)(56)$	(4,0,0,0;0,1)
	σ_v	$\bar{t}_{13} = (1)(24)(3)(5)(6)$	(2,1,0,0;2,0)
	σ_v	$\bar{t}_{14} = (13)(2)(4)(5)(6)$	(2,1,0,0;2,0)
	σ_d	$\bar{t}_{15} = (12)(34)(5)(6)$	(0,2,0,0;2,0)
	σ_d	$\bar{t}_{16} = (14)(23)(5)(6)$	(0,2,0,0;2,0)

[a] The definition of generalized cyclic type is provided in Appendix I.

Consulting Table I, we note that $|D_4| = 8$ and $|C_2| = 2$. The summation extends over all generalized cyclic types which operations in C_3 and D_4 have in common. In this case, these generalized cyclic types are (4,0,0,0;2,0) and (0,2,0,0;0,1), and the summation contains only two terms. The number of operations in D_4 and C_2 having cyclic type $(j_1j,j_2,j_3,j_4;\ k_1,k_2)$ is $h^{D_4}{}_{j_1j_2j_3j_4,k_1k_2}$ and $h^{C_2}{}_{j_1j_2j_3j_4,k_1k_2}$, respectively. For the first term of the summation, $h^{D_4}{}_{4000,20} = 1$, $h^{C_2}{}_{4000,20} = 1$, $\Pi_{i=1}{}^4 j_i! i^{j_i} = 4!1^4 = 24$, and $\Pi_{l=1}{}^2 k_l! l^{k_l} = 2!1^2 = 2$. Therefore the first term equals 48. Following the same procedure, the second term is equal to $2 \cdot 1 \cdot (2!2^2) \cdot (1!2^1) = 32$. Adding these two terms and dividing by $|C_2| \cdot |D_4| = 16$, we find $D_{D_4C_2} = 5$.

The value of $D_{D_4C_2}$ is not in itself a particularly useful piece of information unless it is of help in actually generating a set of formally differentiable reactions. When dealing with permutational isomerization reactions, a complete set of differentiable reactions could be derived from a set of formally distinguishable reactions.[7,16] Formally distinguishable reactions are unfortunately undefined for polytopal isomerization reactions, and other methods must be used to generate the desired reactions. For the present case, we make the following observation: if two operations h_i^{TR} and h_j^{TR} convert the reference isomer into the same permutational isomer of polytopal form T, then h_i^{TR} and h_j^{TR} are nondifferentiable in a chiral environment. Formally, let

$$h_i^{TR}\begin{pmatrix} l \\ s \end{pmatrix}_e^R = \begin{pmatrix} l \\ s \end{pmatrix}_i^T \text{ and } h_j^{TR}\begin{pmatrix} l \\ s \end{pmatrix}_e^R = t_i^{TT}\begin{pmatrix} l \\ s \end{pmatrix}_i^T$$

Then

$$(t_i^{-1})^{TT} h_j^{TR}\begin{pmatrix} l \\ s \end{pmatrix}_e^R = \begin{pmatrix} l \\ s \end{pmatrix}_i^T$$

and therefore

$$h_i^{TR} = (t_i^{-1} \cdot h_j)^{TR}$$

i.e., $h_i = t_i^{-1} \cdot h_j$. Since there are $n_1!n_2!/|D_4| = 6$ permutational isomers of polytopal form D_{4h}, we list these six isomers on the right-hand side of Figure 4b and examine the polytopal isomerization reactions which generate these isomers when acting on the reference isomer of polytopal form C_{2v}. Of these six reactions, only five can be differentiable in a chiral environment. Since $h_6 = t_6 \cdot h_5 \cdot r_2$, the first five reactions listed in Figure 4b serve as a complete set of polytopal isomerization reactions differentiable in a chiral environment.

To determine which of these reactions are chiral, we look at "mirror images" of the five reactions. For example

$$\bar{t}_{12} \cdot h_1 \cdot \bar{r}_4 = (12)(3)(4)(5)(6)$$

When $(12)(3)(4)(5)(6)^{D_4C_2}$ acts on $\binom{l}{s}_e^{C_2}$, it generates the same isomer as does $h_3^{D_4C_2}$ when acting on $\binom{l}{s}_e^{C_2}$. Therefore $(\bar{t}_{12} \cdot h_1 \cdot \bar{r}_4)^{D_4C_2}$ and $h_3^{D_4C_2}$ are nondifferentiable in a chiral environment, indicating that $h_1^{D_4C_2}$ and $h_3^{D_4C_2}$ are enantiomers. We can similarly show that $h_2^{D_4C_2}$ and $h_3^{D_4C_2}$ are enantiomers, and $h_5^{D_4C_2}$ is achiral. Therefore, if we construct the topological representations generated by $h_1^{D_4C_2}$, $h_2^{D_4C_2}$, and $h_5^{D_4C_2}$, we are assured that any other polytopal isomerization reaction must generate one of these three topological representations.

Letting $B = D_{4h}$ and $W = C_{2h}$ in eq A1, we find $D_{D_{3h}C_{2h}} = 2$. Since enantiomeric reactions are nondifferentiable in a totally symmetric environment, the set of reactions $h_1^{D_4C_2}$, $h_2^{D_4C_2}$, and $h_5^{D_4C_2}$ must contain two reactions which are differentiable in a totally symmetric environment. These two reactions are $h_1^{D_4C_2}$ and $h_5^{D_4C_2}$ (or $h_2^{D_4C_2}$ and $h_5^{D_4C_2}$) since $h_1 = h_2 \cdot \bar{r}_3$.

Polytopal Isomerization of Trigonal-Bipyramidal Molecules. In a discussion of topological representations generated by polytopal isomerizations of trigonal-bipyramidal molecules, Muetterties[3,17] examined six different processes, three of which are shown in Figure 5a. Muetterties deduced that these three "classes" were open,[3] since $I_T\delta_T \neq I_R\delta_R$. Using the formalisms developed in this paper, it was found that $I_T\delta_T = I_R\delta_R$ regardless of closure properties. We shall therefore examine the connectivities of these processes in order to account for this discrepancy.

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(16) W. G. Klemperer, *J. Chem. Phys.*, 56, 5478 (1972).

(17) E. L. Muetterties, *J. Amer. Chem. Soc.*, **91**, 4115 (1969).

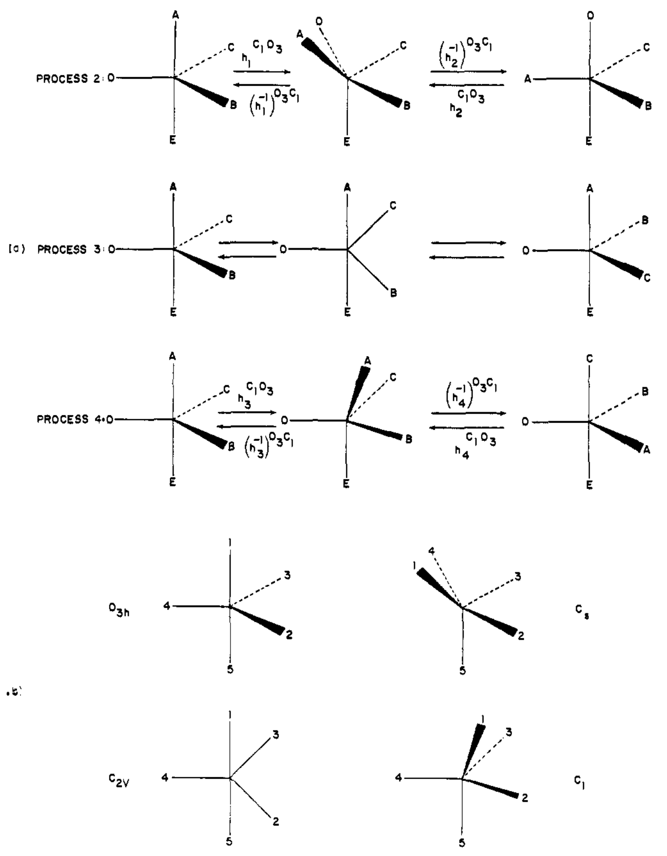

Figure 5. Some polytopal isomerization processes are shown in (a). Indexing of skeletal positions is defined in (b).

In all these examples, $n_1 = 5$ and $n_2 = 0$. The ligand set $\{A, B, C, D, E\}$ is labeled by $\{l_1, l_2, l_3, l_4, l_5\}$ in that order. Also, $\bar{R}$ is always D_{3h}. Labeling the skeletal positions as in Figure 5b, R and $\bar{R}$ consist of

$r_1 = \bar{r}_1 = (1)(2)(3)(4)(5)$
$r_2 = \bar{r}_2 = (1)(234)(5)$
$r_3 = \bar{r}_3 = (1)(243)(5)$
$r_4 = \bar{r}_4 = (15)(2)(34)$
$r_5 = \bar{r}_5 = (15)(3)(24)$
$r_6 = \bar{r}_6 = (15)(23)(4)$
$\bar{r}_7 = (15)(2)(3)(4)$
$\bar{r}_8 = (15)(234)$
$\bar{r}_9 = (15)(243)$
$\bar{r}_{10} = (1)(2)(34)(5)$
$\bar{r}_{11} = (1)(24)(3)(5)$
$\bar{r}_{12} = (1)(23)(4)(5)$

For process 2, $\bar{T} = C_s$ and $T = C_1$ (see Figure 5). Labeling the skeletal positions as in Figure 5b, $t_1 = \bar{t}_1 = (1)(2)(3)(4)(5)$, $\bar{t}_2 = (14)(23)(5)$. The polytopal isomerization reaction $h_1^{C_1D_3} = (1)(2)(3)(4)(5)^{C_1D_3}$ describes the process, and $(h_1^{-1})^{D_3C_1} = (1)(2)(3)(4)(5)^{D_3C_1}$ is the reverse reaction. This reaction is chiral, and the enantiomeric reaction $h_2^{C_1D_3} = (14)(2)(3)(5)^{C_1D_3}$ is also shown in Figure 5a, along with $(h_2^{-1})^{D_3C_1} = h_2^{D_3C_1}$. Accordingly, eq 7 and 8 must be used to calculate connectivities. Since $h_1 = h_1^{-1} = e$

$$|D_3 \cap h_1^{-1}C_1h_1| = |C_1 \cap h_1D_3h_1^{-1}| = |C_1 \cap D_3| = 1$$

and consequently

$$\delta_{D_3} = 2\cdot|D_3| = 12$$

$$\delta_{C_1} = 2\cdot|C_1| = 2$$

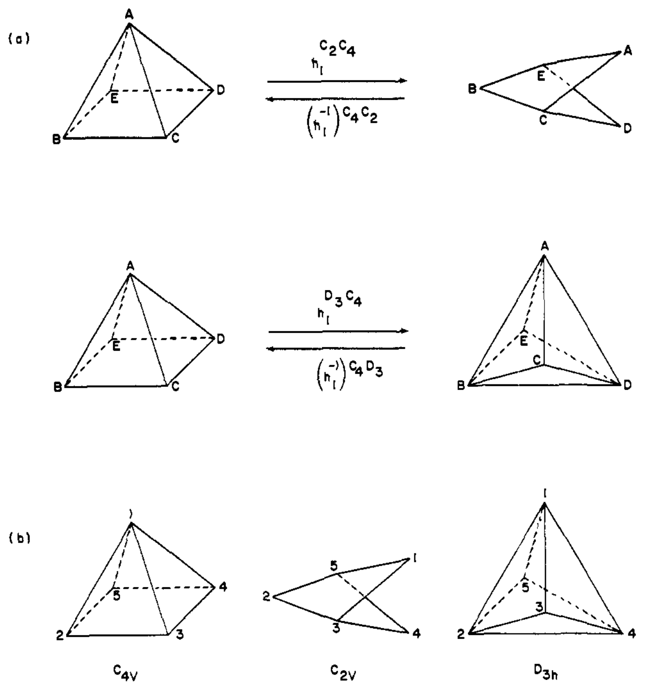

Figure 6. Four polytopal isomerization reactions of $(CH)_5^+$ are given in (a). A, B, C, D, and E represent CH groups. Indexing of skeletal positions is defined in (b).

Also, $I_{D_3} = 5!/6 = 20$ and $I_{C_1} = 5!/1 = 120$. Therefore $I_{D_3}\delta_{D_3} = 20\cdot 12 = 240$ and $I_{C_1}\delta_{C_1} = 120\cdot 2 = 240$. This result differs from Muetterties' in that he found $\delta_{D_3} = 6$, a result which indicates that the chiral nature of $h_1^{C_1D_3}$ was overlooked.

The reader may verify that the polytopal isomerization reaction defined by process 3 is chiral and $I_{D_3} = 20$, $I_{C_2} = 60$, $\delta_{D_3} = 6$, $\delta_{C_2} = 2$, and therefore $I_{D_3}\delta_{D_3} = I_{C_2}\delta_{C_2} = 120$. Again Muetterties finds $\delta_{D_3} = 3$ by neglecting the chiral nature of this process.

Labeling skeletal positions as shown in Figure 5b, we let $h_3^{C_1D_3}$ represent the polytopal isomerization reaction which generates the C_1 intermediate configuration for process 4. This reaction cannot be chiral in the same sense defined above since $\bar{T} = C_1$ contains no improper operations. $I_{D_3}\delta_{D_3} = I_{C_1}\delta_{C_1}$, but since $\delta_{C_1} = 1$, no permutational isomerization reactions of polytopal isomer D_3 are apparently implied. This is unsatisfying since process 4 clearly does lead to permutational isomerization of the trigonal bipyramidal isomers. The "problem" is resolved by realizing that h_3^{TR} and h_4^{TR} are formally differentiable reactions in a chiral environment. These reactions are clearly not symmetry equivalent since one represents a net rotation of a trigonal-bipyramidal face by $\theta \neq 60°$, and the other represents a net rotation of $120 - \theta$. Thus "proper" description of the polytopal isomerization reactions implied by process 4 in terms of the C_1 intermediate configuration demands the use of two differentiable isomerization reactions, $h_3^{C_1D_3}$ and $h_4^{C_1D_3}$.

Permutational Isomerization of $(CH)_5^+$. Stohrer and Hoffmann[18] have suggested that the unique stable structure of the $(CH_5)^+$ cation is square pyramidal, and that permutational isomerization of this species should occur *via* an intermediate C_{2v} configuration instead of a D_{3h} configuration (see Figure 6). Should

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(18) W. Stohrer and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 1661 (1972).

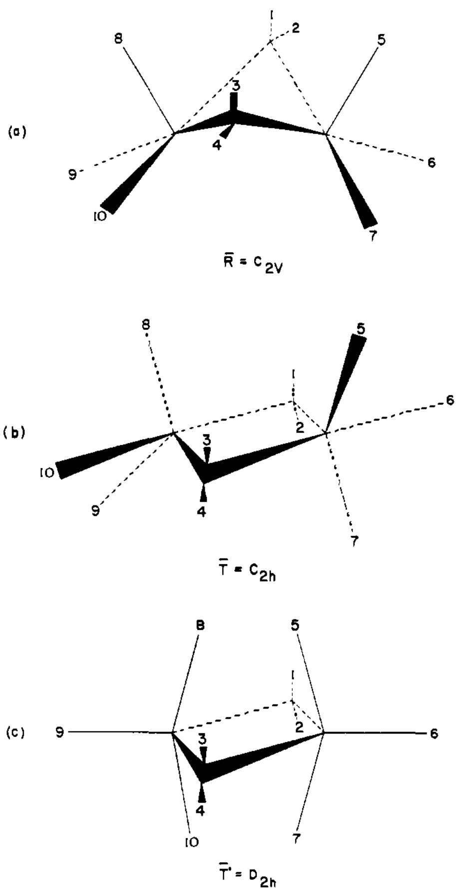

Figure 7. Three skeletal frameworks representing polytopal isomers of molecules $[(CR_3)_2A]_2Fe_2(CO)_6$. The numbers define indexing of the skeletal positions.

Table II. Permutation Group Operations Generated when C_{4v}, C_{2v}, and D_{3h} Act on the Indices of the Skeletal Positions Defined in Figure 6b

Group	Point group operations	Permutation group operation
	E	$r_1 = \bar{r}_1 = (1)(2)(3)(4)(5)$
	C_2	$r_2 = \bar{r}_2 = (1)(24)(35)$
	C_4	$r_3 = \bar{r}_3 = (1)(2345)$
$R = C_4$	C_4^{-1}	$r_4 = \bar{r}_4 = (1)(2543)$
$\bar{R} = C_{4v}$	σ_v	$\bar{r}_5 = (1)(24)(3)(5)$
	σ_v	$\bar{r}_6 = (1)(2)(35)(4)$
	σ_d	$\bar{r}_7 = (1)(23)(45)$
	σ_d	$\bar{r}_8 = (1)(25)(34)$
	E	$t_1 = \bar{t}_1 = (1)(2)(3)(4)(5)$
$T = C_2$	C_2	$t_2 = \bar{t}_2 = (14)(2)(35)$
$\bar{T} = C_{2v}$	σ_v	$\bar{t}_3 = (14)(2)(3)(5)$
	σ_v'	$\bar{t}_4 = (1)(2)(35)(4)$
	E	$t_1' = \bar{t}_1' = (1)(2)(3)(4)(5)$
	C_3	$t_2' = \bar{t}_2' = (124)(3)(5)$
	C_3	$t_3' = \bar{t}_3' = (142)(3)(5)$
	C_2	$t_4' = \bar{t}_4' = (1)(24)(35)$
	C_2	$t_5' = \bar{t}_5' = (14)(2)(35)$
$T' = D_3$	C_2	$t_6' = \bar{t}_6' = (12)(35)(4)$
$\bar{T}' = D_{3h}$	σ_h	$\bar{t}_7' = (1)(2)(35)(4)$
	S_3	$\bar{t}_8' = (124)(35)$
	S_3	$\bar{t}_9' = (142)(35)$
	σ_v	$\bar{t}_{10}' = (1)(24)(3)(5)$
	σ_v	$\bar{t}_{11}' = (14)(2)(3)(5)$
	σ_v	$\bar{t}_{12}' = (12)(3)(4)(5)$

this system ever be subjected to spectroscopic examination, it is probable that even though the postulated polytopal isomerization process takes place, the intermediate C_{2v} configuration will be very short-lived and therefore escape detection. The process could then only be characterized in terms of the permutational isomerization reactions implied by the polytopal isomerization process taking place. We shall therefore investigate the sets of differentiable permutational isomerization reactions implied by each of the two polytopal isomerization processes shown in Figure 6a to see if these pathways might be distinguishable on that basis.

The first process shown in Figure 6a is characterized by $h_1^{C_2C_4} = (1)(2)(3)(4)(5)^{C_2C_4}$. The permutation groups given in Table II are generated by C_2, D_3, C_{2v}, and D_{3h} if skeletal positions are indexed as in Figure 6b. $h_1^{C_2C_4}$ is achiral since $\bar{t}_4 \cdot h_1 \cdot \bar{r}_6 = h_1$. Thus the set of two operations $(h_1^{-1}C_2h_1)^{C_4C_4} = C_2^{C_4C_4}$ contains the permutational isomerization reactions implied by $c_1^{C_2C_4}$. Since

$$\psi^{C_4C_4}(h_1^{C_2C_4}) = \bar{\psi}^{C_4C_4}(h_1^{C_2C_4}) = e + t_2$$

any permutational isomerization reaction implied by this process is nondifferentiable from $t_2^{C_4C_4} = (14)(2)(35)^{C_4C_4}$.

For the second process shown in Figure 6a, $\bar{R} = C_{4v}$ and $\bar{T}' = D_{3h}$. The appropriate permutation groups are given in Table II. $h_1^{D_3C_4} = (1)(2)(3)(4)(5)^{D_3C_4}$ is achiral since $\bar{t}_7' \cdot h_1 \cdot \bar{r}_6 = h_1$, and the set of six operations $(h_1^{-1}D_3h)^{C_4C_4} = D_3^{C_4C_4}$ contains the permutational isomerization reactions of interest. Since $t_1' = r_1$, $t_4' = r_2$, and $t_5' = r_2 \cdot t_2' = t_3' \cdot r_2 = r_2 \cdot t_6' \cdot r_2$, we see that

$$\psi^{C_4C_4}(h_1^{D_3C_4}) = \bar{\psi}^{C_4C_4}(h_1^{D_3C_4}) = 2e + 4t_5'$$

i.e., any permutational isomerization reaction implied by this process is nondifferentiable from $t_5'^{C_4C_4} = (14)(2)(35)^{C_4C_4}$.

Comparing results, we note that $t_5' = t_2$ and therefore both processes in Figure 6a imply the same permutational isomerization reactions of the C_4 polytopal isomer.

Permutational Isomerization of Molecules $[(CR_3)_2A]_2M_2(CO)_6$. Molecules of this type which have been shown to undergo permutational isomerization reactions include $[(CF_3)_2P]_2Fe_2(CO)_6$,[19] $[(CH_3)_2Ge]_2Co_2(CO)_6$,[20] and $[(CH_3)_2P]_2Fe_2(CO)_6$.[21] The stable polytopal form of these molecules is shown in Figure 7a. Skeletal positions 1–4 are occupied by CR_3 ligands, and positions 5–10 are occupied by CO ligands. Different mechanisms have been proposed to describe the permutational isomerization of these molecules. The first, proposed by Adams and Cotton,[20] assumes the C_{2h} intermediate configuration shown in Figure 7b. Dessy, Rheingold, and Howard[21] proposed alternative mechanisms which involve the D_{2h} intermediate shown in Figure 7c. Neither of these intermediate configurations has been detected by nmr spectroscopy. Hence, temperature dependent nmr line-shape simulations using the "jump model" must be based on the permutational isomerization reactions implied by the proposed polytopal isomerization reactions. We therefore examine these permutational isomerization reactions in

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[19] V. J. Grobe, *Z. Anorg. Allg. Chem.*, 361, 32 (1968).

[20] R. D. Adams and F. A. Cotton, *J. Amer. Chem. Soc.*, 92, 5003 (1970).

[21] R. E. Dessy, A. L. Rheingold, and G. D. Howard, *ibid.*, 94, 746 (1972).

order to ascertain whether any or all of the mechanisms may be ruled out on the basis of nmr studies.

The Adams–Cotton mechanism (or AC mechanism) defines the polytopal isomerization reaction $h_1^{TR} = (1)(2)(3)(4)(5)(6)(7)(8)(9)(10)^{TR}$ if skeletal positions are labeled as in Figure 7. The pertinent groups $\bar{R} = C_{2v}$, $R = C_2$, $\bar{T} = C_{2h}$, and $T = C_2$ are presented in Table III.

$$h_2^{TR} = \bar{t}_3^{TT} \cdot h_1^{TR} \cdot \bar{r}_4^{RR} = (14)(23)(576)(89\ 10)^{TR}$$

Table III. Permutation Group Operations Generated When C_{2v}, C_{2h}, and D_{2h} Act on the Indices of the Skeletal Positions Defined in Figure 7

Group	Point group operations	Permutation group operations
	E	$r_1 = \bar{r}_1 = (1)(2)(3)(4)(5)(6)(7)(8)(9)(10)$
$R = C_2$	C_2	$r_2 = \bar{r}_2 = (13)(24)(58)(6\ 10)(79)$
$\bar{R} = C_{2v}$	σ_v	$\bar{r}_3 = (1)(2)(3)(4)(58)(69)(7\ 10)$
	σ_v'	$\bar{r}_4 = (13)(24)(5)(67)(8)(9\ 10)$
	E	$t_1 = \bar{t}_1 = (1)(2)(3)(4)(5)(6)(7)(8)(9)(10)$
$T = C_2$	C_2	$t_2 = \bar{t}_2 = (13)(24)(58)(6\ 10)(79)$
$\bar{T} = C_{2h}$	σ_h	$\bar{t}_3 = (12)(34)(57)(6)(89)(10)$
	i	$\bar{t}_4 = (14)(23)(59)(6\ 10)(78)$
	E	$t_1' = \bar{t}_1' = (1)(2)(3)(4)(5)(6)(7)(8)(9)(10)$
	C_2	$t_2' = \bar{t}_2' = (13)(24)(58)(69)(7\ 10)$
	C_2	$t_3' = \bar{t}_3' = (12)(34)(5\ 10)(69)(78)$
$T' = D_2$	C_2	$t_4' = \bar{t}_4' = (14)(23)(57)(6)(8\ 10)(9)$
$\bar{T}' = D_{2h}$	i	$\bar{t}_5' = (14)(23)(5\ 10)(69)(78)$
	σ	$\bar{t}_6' = (12)(34)(57)(6)(8\ 10)(9)$
	σ	$\bar{t}_7' = (13)(24)(5)(6)(7)(8)(9)(10)$
	σ	$\bar{t}_8' = (1)(2)(3)(4)(58)(69)(7\ 10)$

is a "mirror image" of h_1^{TR}. h_1^{TR} and h_2^{TR} are in fact enantiomers. The set of eight operations $(h_1^{-1}Th_1)^{RR}$, $(h_1^{-1}Th_2)^{RR}$, $(h_2^{-1}Th_1)^{RR}$, and $(h_2^{-1}Th_2)^{RR}$ contains four rotation operations and two pairs of reactions nondifferentiable in a chiral environment, $h_2^{RR} = (14)(23)(576)(89\ 10)^{RR}$ and $(12)(34)(59687\ 10)^{RR} = (r_2 \cdot h_2)^{RR}$, $h_3^{RR} = (14)(23)(567)(8\ 10\ 9)^{RR}$ and $(12)(34)(5\ 10\ 7869)^{RR} = (r_2 \cdot h_3)^{RR}$. Therefore

$$\psi^{RR}(h_1^{TR}) = 4e + 2h_2 + 2h_3$$

h_2^{RR} and h_3^{RR} are shown in Figure 8.

Dessy, Rheingold, and Howard proposed their mechanism in terms of the two polytopal fragments shown in Figure 9. Using the skeletal indices defined in Figure 9, the enantiomeric polytopal isomerization reactions "d" $= (1)(2)(3)(4)(5)(6)(7)^{C_2C_1}$ and "l" $= (1)(2)(3)(4)(5)(67)^{C_2C_1}$ are implied by their mechanism. The reactions d and l may be combined in four different ways to generate polytopal isomerization reactions which interconvert the isomers of polytopal form C_{2v} and D_{2h} shown in Figure 7.

$$dl \equiv h_1^{T'R} = (1)(2)(3)(4)(5)(6)(7)(8)(9)(10)^{T'R}$$

$$ld \equiv h_5^{T'R} = (1)(2)(3)(4)(5)(67)(8)(9\ 10)^{T'R}$$

$$dd \equiv h_7^{T'R} = (1)(2)(3)(4)(5)(6)(7)(8)(9\ 10)^{T'R}$$

$$ll \equiv h_8^{T'R} = (1)(2)(3)(4)(5)(67)(8)(9)(10)^{T'R}$$

$h_1^{T'R}$ and $h_5^{T'R}$ are achiral reactions nondifferentiable in a chiral environment, while $h_7^{T'R}$ and $h_8^{T'R}$ are enantiomers. $h_1^{T'R}$ and $h_7^{T'R}$ are differentiable in a chiral environment. (One can easily show that a chiral reaction and an achiral reaction must always be differentiable in a chiral environment.) Therefore, Dessy, Rheingold, and Howard actually proposed two nonequivalent polytopal isomerization processes:

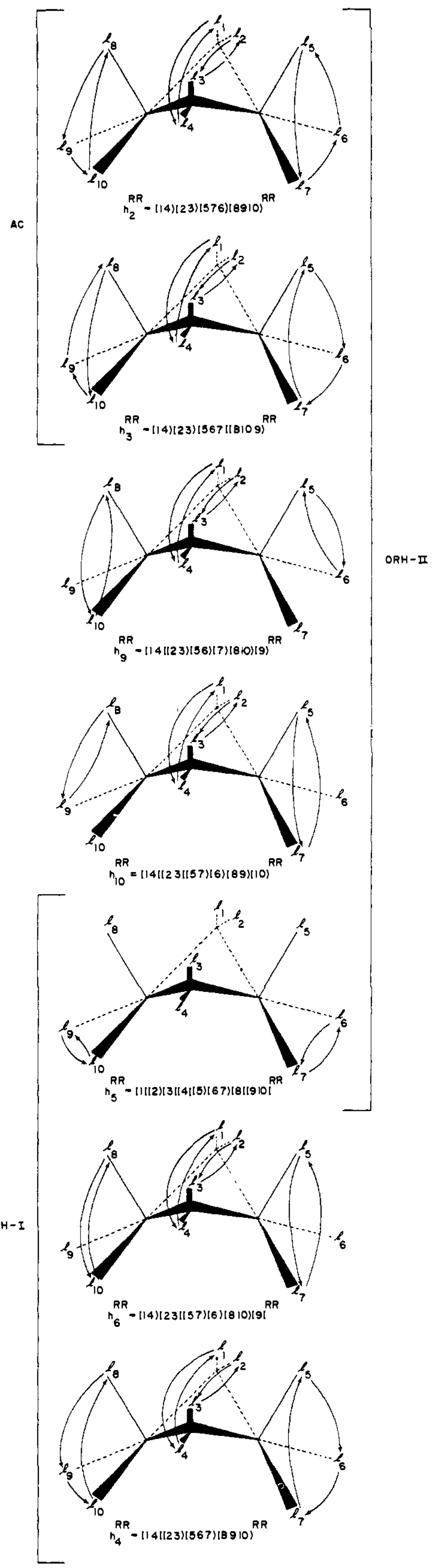

Figure 8. Seven permutational isomerization reactions of molecules $[(CR_3)_2A]_2Fe_2(CO)_6$. Skeletal positions are indexed as in Figure 7a. The l_i's are ligand labels. The arrows represent permutation operations, not mechanistic pathways.

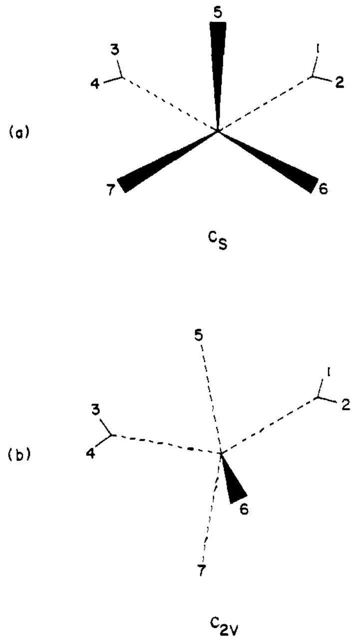

Figure 9. Two polytopal fragments: (a) is derived from Figure 7a; (b) is derived from Figure 7c. Numbers are indices of the skeletal positions.

one, which we call DRH-I, is characterized by $h_1^{T'R}$, while the other, DRH-II, is characterized by $h_7^{T'R}$. The reader may verify that

$$\psi^{RR}(h_1^{T'R}) = e + h_4 + h_5 + h_6$$

and

$$\psi^{RR}(h_7^{T'R}) = 4e + 2h_2 + 2h_3 + 4h_5 + 2h_9 + 2h_{10}$$

where

$$h_4^{RR} = (14)(23)(567)(89\ 10)^{RR}$$

$$h_5^{RR} = (1)(2)(3)(4)(5)(67)(8)(9\ 10)^{RR}$$

$$h_6^{RR} = (14)(23)(57)(6)(8\ 10)(9)^{RR}$$

$$h_9^{RR} = (14)(23)(56)(7)(8\ 10)(9)^{RR}$$

and

$$h_{10}^{RR} = (14)(23)(57)(6)(89)(10)^{RR}$$

h_2^{RR} and h_3^{RR} were defined above. All these reactions are shown in Figure 8.

We now compare the sets

$$\bar{\psi}^{RR}(h_1^{TR}) = 4e + 4h_2$$

$$\bar{\psi}^{RR}(h_7^{T'R}) = e + h_4 + h_5 + h_6$$

and

$$\bar{\psi}^{RR}(h_7^{T'R}) = 4e + 4h_2 + 4h_5 + 4h_9$$

The reactions h_2^{RR}, h_4^{RR}, h_5^{RR}, h_6^{RR}, and h_9^{RR} are all formally differentiable in a totally symmetric environment. Therefore, line-shape analysis of temperature-dependent nmr spectra of a suitable model compound may enable one to establish which one (if any) of these mechanisms are consistent with experiment. $[(CH_3)_2{}^{31}P]_2Fe_2({}^{13}CO)_6$ might be suitable, assuming that all $^{13}C-^{31}P$ spin couplings are experimentally observed and resolved. In practice, such a decision may of course be impossible. The important point is that symmetry arguments do not rule out the possibility as was the case for the last example.

Thus far, we have assumed that "memory effects" are ruled out. Although intermediate situations may exist, there is the extreme case where the "memory effect" is complete; *i.e.*, the intermediate polytopal configurations must have connectivities of two. In this case, the AC mechanism implies h_2^{RR}, DRH-I implies h_6^{RR}, and DRH-II implies h_9^{RR}. These three reactions are formally differentiable in a totally symmetric environment.

Appendix I

In this appendix, a formula is presented which counts double cosets Bh_iW in the permutation group $H \equiv S_{n_1} + S_{n_2}$. B and W are arbitrary subgroups of H. For computational purposes, permutations in B and W are described by their generalized cyclic types. The generalized cyclic type of a permutation $h_k \epsilon H$ is $(j_1, j_2, \ldots, j_{n_1};\ k_1, k_2, \ldots, k_{n_2})$ if h_k contains j_i cycles of length i which permute the numbers one through n_1 among themselves and k_l cycles length l which permute the numbers $n_1 + 1$ through $n_1 + n_2$ among themselves. $h^B{}_{j_1j_2\ldots j_{n_1},k_1k_2\ldots k_{n_2}}$ and $h^W{}_{j_1j_2\ldots j_{n_1},k_1k_2\ldots k_{n_2}}$ are the numbers of permutations in B and W, respectively, having cyclic type $(j_1, j_2, \ldots, j_{n_1};\ k_1, k_2, \ldots, k_{n_2})$. If D_{BW} is defined as the number of double cosets Bh_iW in H, then

$$D_{BW} = \frac{1}{|B||W|}\sum_{B,W}(h^B{}_{j_1j_2\ldots j_{n_1},k_1k_2\ldots k_{n_2}}) \times (h^W{}_{j_1j_2\ldots j_{n_1},k_1k_2\ldots k_{n_2}})\prod_{i=1}^{n_1}(j_i!i^{j_i})\prod_{l}^{n_2}(k_l!l^{k_l}) \quad \text{(A1)}$$

where the summation is made over all cyclic types found in B and W. This formula is a trivial extension of a theorem by de Bruijn[22] and no proof is provided. It may be derived following the procedures used in Appendix II of ref 7. Since eq A1 is symmetric with respect to permutation of B and W, $D_{BW} = D_{WB}$. If $B = W$, eq A1 reduces to eq A8 of ref 7.

Appendix II

Here, formulas for calculating connectivities are provided. We choose an arbitrary permutational isomer of polytopal form R which is defined by the set of $\binom{l}{s}^R$ matrices $R^{RR}\binom{l}{s}_i^R$. The polytopal isomerization reaction h_o^{TR} and its "mirror image" h_p^{TR} convert this permutational isomer to the permutational isomers of polytopal form T defined by $\binom{l}{s}^T$ matrices contained in the sets

$$T^{TT}h_o^{TR}R^{RR}\binom{l}{s}_i^R$$

and

$$T^{TT}h_p^{TR}R^{RR}\binom{l}{s}_i^R$$

Two of these $\binom{l}{s}^T$ matrices, $\binom{l}{s}_j^T$ and $\binom{l}{s}_k^T$ define the same permutational isomer if

$$\binom{l}{s}_k^T = t_i^{TT}\binom{l}{s}_j^T$$

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[22] N. G. de Bruijn in "Applied Combinatoral Mathematics," E. Beckenbach, Ed., Wiley, New York, N. Y., 1964, p 166.

for some $t_i^{TT} \epsilon T^{TT}$. In other words, the number of right cosets Th_i contained in the sets of operations Th_oR and Th_pR equals the connectivity δ_R.

We first assume that h_o^{TR} is achiral. Then by definition, $Th_oR = Th_pR$. Thus δ_R is the number of right cosets Th_i in Th_oR. This number is calculated by eq A2.[23]

$$\delta_R = \frac{|R|}{|R \cap h_o^{-1}Th_o|} \tag{A2}$$

If h_o is chiral and $h_p = \bar{l}_o \cdot h_o \cdot \bar{r}_o$, then the sets of operations Th_oR and Th_pR are mutually exclusive. We shall demonstrate that the number of right cosets Th_i in Th_oR equals the number of right cosets Th_j in Th_pR; *i.e.*, eq A3 holds.

$$\delta_R = \frac{2|R|}{|R \cap h_o^{-1}Th_o|} \tag{A3}$$

We put the elements of h_oR and h_pR into a 1:1 correspondence by associating $h_o \cdot r_n$ with $\bar{l}_o \cdot h_o \cdot r_n \cdot \bar{r}_o$. Proof of eq A3 involves showing that

$$h_o \cdot r_n = t_i \cdot h_o \cdot r_m$$

for some $t_i \epsilon T$ if and only if

$$\bar{l}_o \cdot h_o \cdot r_n \cdot \bar{r}_o = t_j \cdot \bar{l}_o \cdot h_o \cdot r_m \cdot \bar{r}_o$$

for some $t_j \epsilon T$. This relation holds since: (i) for any given t_j and $\bar{l}_o$, $t_j \cdot \bar{l}_o = \bar{l}_o \cdot t_k$ for some $t_k \epsilon T$ and, therefore, if

$$\bar{l}_o \cdot h_o \cdot r_n \cdot \bar{r}_o = t_j \cdot \bar{l}_o \cdot h_o \cdot r_m \cdot \bar{r}_o$$

then

$$\bar{l}_o \cdot h_o \cdot r_n \cdot \bar{r}_o = \bar{l}_o \cdot t_k \cdot h_o \cdot r_m \cdot \bar{r}_o$$

and consequently

$$h_o \cdot r_n = t_k \cdot h_o \cdot r_m$$

for some $t_k \epsilon T$. (ii) $h_o \cdot r_n = t_i \cdot h_o \cdot r_m$ implies that

$$\bar{l}_o \cdot h_o \cdot r_n \cdot \bar{r}_o = \bar{l}_o \cdot t_1 \cdot h_o \cdot r_m \cdot \bar{r}_o$$

Since $\bar{l}_o \cdot t_i = t_j \cdot \bar{l}_o$ for some $t_j \epsilon T$

$$\bar{l}_o \cdot h_o \cdot r_n \cdot \bar{r}_o = t_j \cdot \bar{l}_o \cdot h_o \cdot r_m \cdot \bar{r}_o$$

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(23) For a proof, see ref 10. Note that Hall uses a different convention for naming right and left cosets from that used here.

Calculated and Observed Electronic Transitions in Organolithium Aggregates

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Abstract: The ultraviolet spectra of ethyl-, *n*-butyl-, *sec*-butyl-, and *tert*-butyllithium have been observed and found to have λ_{max} of 215 and 203 nm for ethyl (vapor phase) $\epsilon \sim 10^3$; *n*-butyl, λ_{max} 210 nm, ϵ 5.2 × 10^2 (hexane solution); *sec*-butyl, λ_{max} 206 nm (vapor phase); and *tert*-butyl, λ_{max} ~190 nm, $\epsilon \sim 10^3$ (vapor phase). The energies of the electronic transitions have been determined from CNDO/2 calculations on idealized tetrameric and hexameric methyllithium and on the basis of these transitions were predicted at 10.0 eV (124 nm) and at 7.26 eV (171 nm), respectively, in reasonable agreement with observed values.

In a review on organolithium compounds, Brown[2a] reported that alkyllithiums do not absorb in the ultraviolet region. This conclusion was based mainly on the work of Waack and Doran[2b] who studied a series of alkyllithium derivatives in tetrahydrofuran solutions and observed only end absorption.

Molecular orbital calculations by Weiss and Lucken[3] predict that the methyllithium tetramer should have a transition between the highest occupied molecular orbital (t_2) and the lowest unoccupied molecular orbital (a_1) occurring about 240 nm. More sophisticated calculations by Cowley and White[4] using SCC and CNDO/1 methods were used to predict transitions at 403 and 100.6 nm, respectively, for the methyllithium tetramer.

Oliver, *et al.*,[5] have reported a transition for *n*-butyllithium in hexane occurring at λ_{max} 220 nm, while Glaze and Brewer[6] have observed a transition for ethyllithium in isooctane with λ_{max} 210 nm. Due to the extreme reactivity of these compounds and the difficulty in obtaining solvents which are completely free of moisture, oxygen, and olefinic impurities, these results have been viewed with skepticism (see for instance the referee's comment in ref 6).

In an effort to establish whether these reported transitions were due to the alkyllithium species both vapor phase and solution studies of the ultraviolet spectra of organolithium derivatives were initiated. Additional molecular orbital calculations were carried out using the CNDO/2 method since it is reported that these calculations give better results than the earlier CNDO/1 scheme.[7]

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