Topological Analysis of Polytopal Rearrangements. Sufficient Conditions for Closure

Sir:

Isomerization in molecular aggregates may occur by traverse of two related geometries.[1] Therein, topological analysis has been defined[2] and attempted[2,3] but not incisively. Analysis of the nine-atom family has provided insight in assessing *sufficient* conditions for closure (possible traverse of all isomers)[2] of a stereochemical class.

The prevailing, idealized polytopal[2] form in nine-coordinate complexes and in polyhedral boranes is the symmetrically tricapped prism (D_{3h}).[1,4] Here, isomerization may occur (Figure 1) through a capped square antiprismatic (C_{4v}) transitional polytope.[1,5]

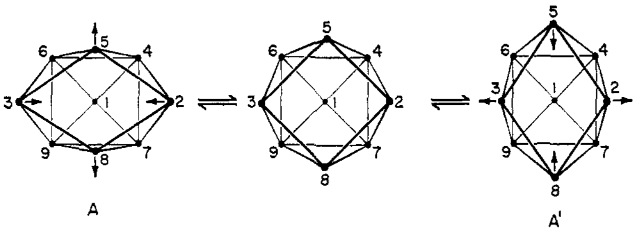

Figure 1. Polytopal rearrangement of the D_{3h}-symmetrical tricapped trigonal prism *via* a C_{4v}-monocapped square antiprism. The permutation for A → A′ is even: $\begin{pmatrix}123456789\\158639427\end{pmatrix}$ = (1) (2538) (4697).

The equal $I \cdot \delta$ (isomer count × connectivity) products of the D_{3h} $[(9!/6)\cdot 3]$ and C_{4v} $[(9!/4)\cdot 2]$ forms satisfy the necessary connected graph requirements for closure. However, closure of the class does not obtain. The rearrangement outlined in Figure 1 comprises an even permutation, yet the group required for generation of all D_{3h} (or C_{4v}) isomers is composed of odd and even permutations.[6] Hence all isomers cannot be traversed by this mechanism. This D_{3h}-C_{4v} stereochemical class is composed of two disjoint groups. The permutation for enantiomer traverse (A → $\bar{\mathrm{A}}$) is odd and disallowed, *i.e.*, this chain (c_E) is not an element of either group. The disjoint groups are isomorphic in that enantiomers have a 1:1 correspondence in their respective groups. In the groups, there are subcycles[2] of order 18, 21, 27, 35, and 36.

An alternative rearrangement through a C_{2v} intermediate suffers a lack of closure for the same reason as above; *cf.* Figure 2. This analysis underscores the importance of the nine-atom family for stereochemical studies. Curiously, this nine-atom family is the only one in the series through 12[1–3] in which class closure is not achieved with a reasonable intermediate. Many of the families have been discussed earlier.[1–3] Those that have not include seven-atom[1] pentagonal bipyramid ⇌ C_{2v} capped trigonal prism ($c_E = 8$); ten-atom[1] symmetrical bicapped square antiprism ⇌ C_{2v}; and eleven-atom C_{2v} ⇌ C_s (Figure 3) or C_{5v}.[1] In these specific classes, the rearrangements meet all the necessary conditions for closure; *i.e.*, the group operations are even–odd and the $I \cdot \delta$ products in each set are equivalent.

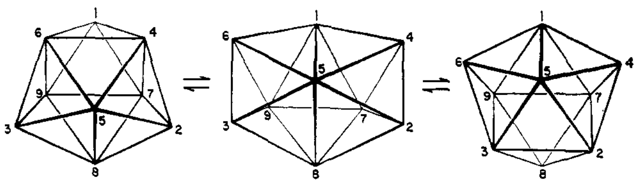

Figure 2. Polytopal rearrangement of the D_{3h}-symmetrical tricapped trigonal prism through a C_{2v} intermediate. The rearrangement is an even permutation.

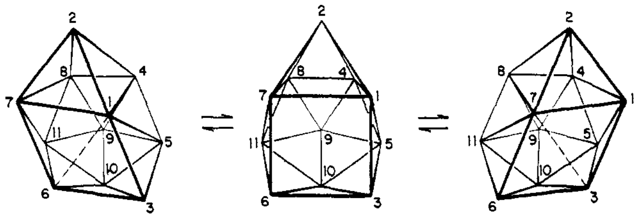

Figure 3. Possible polytopal rearrangement in the 11-atom system with traverse of the C_{2v} and C_s forms; the C_{2v} polytope appears to be the more stable form.[1]

A closed stereochemical class requires (1) the connected graph condition of $I \cdot \delta$ product equality and (2) an operation that is an odd permutation *if* the group of all permutations representing the isomers is even–odd. A further condition must be met in the special polytopes of the planar or cubic groups. If n orthogonal planes of symmetry are present in an n-dimensional polytope and these are maintained in the transitional polytope, class closure cannot be achieved, thus the trivial planar problem of D_{4h} ⇌ D_{2h} wherein the three D_{4h} (general case) isomers are isolated. In the icosahedron ⇌ cuboctahedron ($I \cdot \delta$ products are equivalent and the operations are even–odd), three orthogonal planes of symmetry are maintained, disallowing certain permutations; antipodal vertex relations must be maintained.[2] Each group contains a c_E chain of order eight.

Any stereochemical class can be defined by graph analysis, but this becomes unwieldy for the larger x aggregates. The more elegant approach is through group theory, and this may yield analytical expressions for the order and degeneracy of group elements, *e.g.*, chains (c_E). In addition, identification of proper subgroups may permit for the large aggregates a factorization that would allow two- or three-dimensional topological representations of the subgroups. This approach is being pursued, and isomerization in the

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(1) For a general discussion, *cf.* E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, Inc., New York, N. Y., 1968, Chapter III.

(2) E. L. Muetterties, *J. Am. Chem. Soc.*, **91**, 1636 (1969).

(3) E. L. Muetterties, *ibid.*, **90**, 5097 (1968).

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

(5) F. Klanberg and E. L. Muetterties, *Inorg. Chem.*, **5**, 1955 (1966).

(6) In any group of permutations, either all or exactly half the permutations are even. Note that in addition to the permutation defined by the rearrangement the permutations associated with rotations of the polyhedron must be considered (these are all even in D_{3h}). An example is the RC_3 or face rotation rearrangement for an octahedron. The rearrangement is an even permutation, but a C_4 rotation is odd; this latter operation permits class closure in O_h *via* a trigonal prismatic intermediate.

nine-atom class is being studied with substituted polyhedral boranes.

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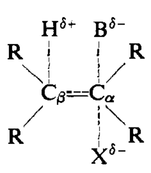
Evidence against the Putative E2C Mechanism of Olefin-Forming Elimination

Sir:

It has been known since 1956 that certain anions which are comparatively weak as bases toward hydrogen are quite effective in provoking elimination from alkyl halides and arenesulfonates.[1,2] Examples are mercaptide ions in alcohols and chloride ion in acetone. These are strong nucleophiles toward carbon, and some authors have attributed their surprising efficacy as elimination reagents to partial covalent interaction of the base (nucleophile) with C_α in the transition state.[2-5] Transition states such as **1** have been suggested, and this



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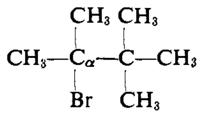
sort of mechanism has been dubbed "E2C."[4]

However, other workers have argued from experimental evidence against such explanations.[7,8]

Any mechanism which required covalent interaction of the base (nucleophile) with C_α in order to make the transition state energetically accessible should be sensitive to steric hindrance of C_α. In 2-bromo-2,3,3-trimethylbutane (**2**), C_α is both tertiary and neopentylic, and thus exceptionally shielded from nucleophilic attack.



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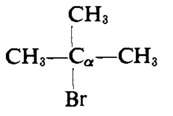

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We have studied the kinetics of chloride ion induced olefin-forming elimination from **2** and from *t*-butyl bromide (**3**), in acetone and in 1,4-dioxane. Structurally, the difference between **2** and **3** is analogous to the difference between ethyl and neopentyl bromides. Ethyl bromide is 240,000 times more reactive than neopentyl bromide in SN2 reactions with $NaOC_2H_5$ in ethanol,[9] and 38,000 times more reactive with lithium chloride in acetone;[10] these data suggest the extent to which **2** should undergo elimination more slowly than **3** if the E2C mechanism prevailed.

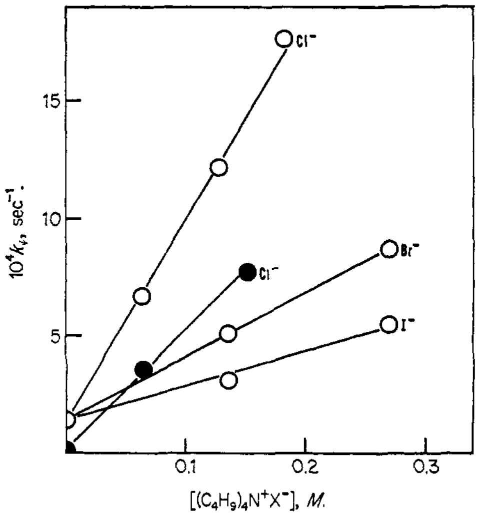

Figure 1. Pseudo-first-order rate coefficients for elimination from **2** (open circles) and from **3** (filled circles), in acetone solution at 69.9°, as functions of tetrabutylammonium halide concentration. The halide ions involved are indicated.

In our rate studies, **2** or **3** (*ca.* 0.02 *M*) was allowed to react with excess tetrabutylammonium chloride, bromide, or iodide in dry acetone or dioxane in the presence of sufficient 2,6-lutidine to neutralize the hydrogen halide generated in the elimination reaction.[4,6] The progress of reaction was followed by acid–base titration. Good linear kinetic plots were obtained. The olefin from **2** was in all cases 2,3,3-trimethyl-1-butene.

The results for acetone solvent at 69.9° are presented in Figure 1. Rates of reaction of both substrates with chloride ion increase linearly with $R_4N^+Cl^-$ concentration; the slopes represent second-order rate coefficients and are $8.8 \times 10^{-3}\ M^{-1}\ sec^{-1}$ for **2** and $5.20 \times 10^{-3}\ M^{-1}\ sec^{-1}$ for **3**.[11] Thus *the highly hindered substrate is actually more reactive than the less hindered one*, by a factor of nearly two. Also, it is noteworthy that the halide ions stand in the reactivity order: $Cl^- > Br^- > I^-$.[12]

The results for dioxane solvent at 69.9° are shown in Figure 2. The picture is substantially the same as in acetone. The second-order rate coefficients (for reaction with $(C_4H_9)_4N^+Cl^-$) are $3.92 \times 10^{-3}\ M^{-1}\ sec^{-1}$ for **2** and $2.44 \times 10^{-3}\ M^{-1}\ sec^{-1}$ for **3**. Again, the highly hindered **2** reacts nearly twice as fast as *t*-butyl bromide.

Solvolysis rates (which are independent of 2,6-lutidine concentration) are low in acetone and particularly low in dioxane. In both solvents, solvolysis of **2** is about tenfold faster than of **3**; rate coefficients are $1.42 \times 10^{-4}\ sec^{-1}$ for **2** and $0.16 \times 10^{-4}\ sec^{-1}$ for **3** in acetone; in dioxane, they are $6.5 \times 10^{-6}\ sec^{-1}$ for **2** and $0.61 \times 10^{-6}\ sec^{-1}$ for **3**. The greater solvolytic reactivity of **2** in both solvents is attributed to steric acceleration, arising from compressions in **2** between the bromine atom and methyl groups.

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[1] P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 41 (1956).

[2] S. Winstein, D. Darwish, and N. J. Holness, *J. Amer. Chem. Soc.*, 78, 2915 (1956).

[3] D. N. Kevill, G. A. Coppens, and N. H. Cromwell, *J. Org. Chem.*, 28, 567 (1963).

[4] A. J. Parker, M. Ruane, G. Biale, and S. Winstein, *Tetrahedron Lett.*, 2113 (1968).

[5] The early hypothesis of "merged substitution and elimination"[2] is abandoned in recent publications of Winstein.[4,6]

[6] S. Winstein, "Chimica Teorica," Accademia Nazionale dei Lincei, Rome, Italy, 1965, p 327.

[7] D. J. McLennan, *J. Chem. Soc.*, *B*, 705, 709 (1966).

[8] J. F. Bunnett and E. Baciocchi, *J. Org. Chem.*, 32, 11 (1967).

[9] I. Dostrovsky and E. D. Hughes, *J. Chem. Soc.*, 157 (1946).

[10] E. D. Hughes, C. K. Ingold, and J. D. H. Mackie, *ibid.*, 3173 (1955).

[11] Winstein[6] reports that reaction of **3** with chloride ion at 50° gives *ca.* 3% *t*-butyl chloride.

[12] Ion pairing for tetrabutylammonium halides in acetone is much less than for alkali metal halides: S. Winstein, L. G. Savedoff, S. Smith, I. D. R. Stevens, and J. S. Gall, *Tetrahedron Lett.*, No. 9, 24 (1960).