Topological Representation of Permutational Isomerization Reactions

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Abstract: Topological representations describing molecules undergoing permutational isomerization reactions are defined in detail. A theorem is proved which places an upper limit on the number of permutational isomerization reactions which generate different topological representations for a given stereochemical system. It is shown how this result may be used to relate various stereochemical properties of molecules undergoing permutational isomerization reactions.

In 1967, a generalized mathematical formulation was presented which provided homological description of chemical reaction networks.[2] It was shown how, in general, algebraic complexes may be used to describe chemical reaction networks and how, in particular, a one-dimensional simplicial complex (a graph) may be used to describe a system of interconverting chemical isomers. Similar chemical application of graphs was first confined to complex organic systems,[3] but, more recently, graphs have been used to describe chemical isomerization reactions of highly symmetric molecules. Various names have been used for these graphs, but the term "topological representation"[4] shall be used here, keeping in mind that a topological representation is simply a graph where the points represent chemical species (isomers) and the lines represent chemical reactions (isomerizations). Perhaps the most thoroughly studied system of isomeric species is that of permutational isomers[5] which interconvert *via* permutational isomerization reactions.[6] Many topological representations have been constructed for these systems.[7] However, since these graphs were constructed in an unsystematic fashion, there has been no convenient way of ascertaining whether or not all the possible topological representations have been constructed for a given system. In this paper, it will be shown that for the general case of a symmetric molecule with n skeletal positions and n unidentate substituents, a definite upper limit can be placed on the number of permutational isomerization reactions which generate different topological representations.

Directed Topological Representations

Permutational isomers are "chemical compounds which have in common the same molecular skeleton and set of ligands, differing only by the distribution of the ligands on the skeletal positions."[5] A set of indexed labels, $L_l = \{l_1, l_2, \ldots, l_n\}$, is assigned to the ligands[8] and a set of indexed labels, $\chi_s = \{s_1, s_2, \ldots, s_n\}$, is assigned to the skeletal positions. A permutational isomer may be described by a 2 × n matrix

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

where the top row lists the ligand indices in an increasing sequence, and below each ligand index is written the index of the skeletal position which that ligand occupies. Figure 1 illustrates the use of these definitions for a trigonal-bipyramidal molecule. If we index the skeletal positions as in Figure 1a and label ligand A with l_1, B with l_2, C with l_3, D with l_4, and E with l_5, the isomer in Figure 1b is described by

$$\begin{pmatrix} l \\ s \end{pmatrix} = \begin{pmatrix} 12345 \\ 52134 \end{pmatrix}$$

We now consider the group S_n which includes all $n!$ permutations of n objects. Let any permutation[9] $p_i \epsilon S_n$ operate on the skeletal indices listed in the bottom row of an $\binom{l}{s}$ matrix. The effect is either to generate a new isomer (Figure 2a) or to rotate the molecule in space (Figure 2b). Operations of the former type are called *permutational isomerization reactions;* rotational operations of the latter type are denoted r_i and are elements of the subgroup R of S_n. If R' is the proper rotational subgroup of the molecular point group, then R is that permutation group whose elements represent the operations in R' and operate on the indices of the skeletal positions. The arrows drawn on the reactant isomers in Figure 2 do not define physical motions of the ligands but merely provide a convenient description of a permutation operation. For example, the arrows

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(2) P. H. Sellers, *SIAM J. Appl. Math.*, **15**, 13 (1967).

(3) A. T. Balaban, D. Fărcaşiu, and R. Bănică, *Rev. Roum. Chim.*, 11, 1205 (1966).

(4) E. L. Muetterties, *J. Amer. Chem. Soc.*, **91**, 1636 (1969).

(5) I. Ugi, D. Marquarding, H. Klusacek, G. Gokel, and P. Gillespie, *Angew. Chem.*, **82**, 741 (1970); *Angew. Chem., Int. Ed. Engl.*, **9**, 703 (1970).

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

(7) For a review, see E. L. Muetterties, *Rec. Chem. Progr.*, **31**, 51 (1970).

(8) It is assumed throughout this paper that all permutational isomers of a molecule have the same molecular point group. For the present discussion, this means that all ligands must be identical and distinguishable only by their labels. If the ligands are not all identical but are very similar in that the different isomers have skeletal frameworks which deviate only slightly from an idealized skeletal framework, then discussion may proceed by using the point group of the idealized skeletal framework. When ligands are not all identical, discretion must be used in defining an idealized skeletal framework; if the skeletal frameworks of two isomers are significantly different, then the isomers are polytopal isomers,[4] not permutational isomers, and the present treatment may not be employed. The word "ligand" is interpreted in the broadest sense to include any type of substituent.

(9) Standard permutation notation is used throughout this paper.[10] For example, (123)(4)(5) means 1 is to be replaced by 2, 2 is to be replaced by 3, 3 is to be replaced by 1, and 4 and 5 remain fixed. All products of operations are read from right to left.

(10) W. Ledermann, "Introduction to the Theory of Finite Groups," Interscience, New York, N. Y., 1961, p 66.

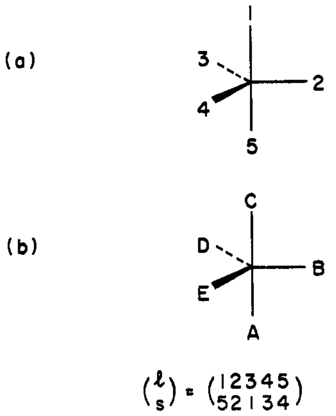

Figure 1. The illustration (a) defines a set of indexed skeletal positions for a trigonal-bipyramidal molecule; (b) shows a set of ligands distributed on the skeletal positions. The matrix defines the indices of the ligand labels.

describing p_i = (1253)(4) mean "the ligand in position 1 is moved to position 2, the ligand in position 2 is moved to position 5, the ligand in position 5 is moved to position 3, and the ligand in position 3 is moved to position 1."

Define a reference isomer[5]

$$\begin{pmatrix} l \\ s \end{pmatrix}_e \equiv \begin{pmatrix} 123\ldots n \\ 123\ldots n \end{pmatrix}$$

then all other isomers are defined by letting permutations $p_i \epsilon S_n$ operate on the reference isomer. For any $p_i \epsilon S_n$, the set of operations $R\cdot p_i \equiv \{r_1\cdot p_i, r_2\cdot p_i, \ldots, r_{|R|}\cdot p_i\}$, where $|R|$ is the order of R, is called a right coset of R in S_n. All the operations in this coset generate the same isomer when acting on the reference isomer. Choose a $p_j \epsilon S_n$ such that $p_j \notin R\cdot p_i$. Then the right coset $R\cdot p_j \equiv \{r_1\cdot p_j, r_2\cdot p_j, \ldots, r_{|R|}\cdot p_j\}$ describes an isomer different from that represented by $R\cdot p_i$. This procedure of generating right cosets is continued until each permutation in S_n has been assigned to a coset. For purposes of illustration, let the elements of each right coset be a row in a matrix

$$\begin{pmatrix} r_1\cdot p_1 & r_2\cdot p_1 \cdots & r_{|R|}\cdot p_1 \\ r_1\cdot p_2 & r_2\cdot p_2 \cdots & r_{|R|}\cdot p_2 \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ r_1\cdot p_{n!/|R|} & r_2\cdot p_{n!/|R|} \cdots & r_{|R|}\cdot p_{n!/|R|} \end{pmatrix}$$

This matrix will have $|R|$ columns and $n!$ elements. Hence the number of rows, *i.e.*, the number of different right cosets, is $n!/|R|$. We arbitrarily select one element from each coset and combine all these elements to form a set C. Each $c_i \epsilon C$ represents a unique permutational isomer; C is called the set of *coset representatives.*

Next consider a set of $n!/|R|$ points, where each point represents a permutational isomer and is labeled by an element $c_i \epsilon C$. Let directed lines (arrows) connecting these points represent permutational isomerization reactions; *i.e.*, a directed line passes from c_i to c_j if and only if a permutational isomerization reaction p_0 implied by some rearrangement mechanism converts the isomer represented by c_i into the isomer represented by c_j. By these definitions, a directed line passes from c_i to c_j if and only if eq 1 holds for some $r_k, r_l \epsilon R$.

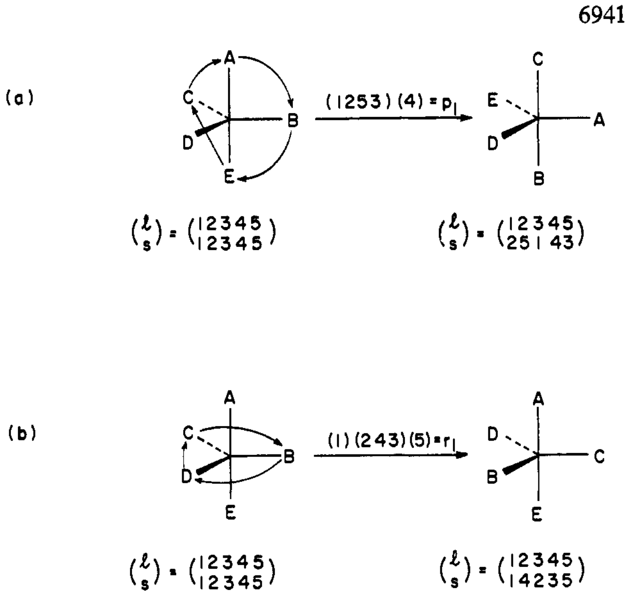

Figure 2. The illustration (a) describes a permutational isomerization reaction, p_i; (b) describes a proper rotation, r_i. Skeletal positions and ligands are labeled as in Figure 1. Permutations always operate on the indices of the skeletal positions.

$$p_0\cdot r_k\cdot c_i = r_l\cdot c_j \tag{1}$$

Such a graph, consisting of points and directed lines, is called a *directed topological representation.* The adjective "directed" is included to emphasize that a directed line pointing from c_i to c_j does not in general imply a directed line pointing from c_j to c_i. More precisely, the fact that eq 1 holds does not imply that an equation $p_0\cdot r_m\cdot c_j = r_n\cdot c_i$ holds for some $r_m, r_n \epsilon R$.

Differentiable Permutational Isomerization Reactions

A rearrangement mechanism does not in general uniquely define a permutational isomerization reaction. This is because a mechanism describes the pathway of a rearrangement while a permutational isomerization reaction defines a rearrangement solely in terms of a reactant isomer (initial configuration) and a product isomer (final configuration), ignoring any intermediate configurations. Figure 3 shows two permutational isomerization reactions, (1453)(2) and (123)(45), either of which may be chosen as a permutational isomerization reaction implied by the Berry mechanism.[11] It also emphasizes that the arrows used to describe permutational isomerization reactions do not unambiguously define physical motions.

If directed topological representations are well defined, then two permutations p_0 and p_0' must generate the same directed topological representation if they are implied by the same mechanism. We assume of course that the connectivity[4] of any intermediate configuration implied by the mechanism is two. Specifically, given two permutations p_0 and p_0' there exists a relationship between p_0 and p_0' that will establish whether or not their respective directed topological representations T and T' are identical. The following theorem states such a relationship.

Theorem. Let C be a set of coset representatives. Let T and T' be two directed topological representations

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(11) R. S. Berry, *J. Chem. Phys.*, 32, 933 (1960).

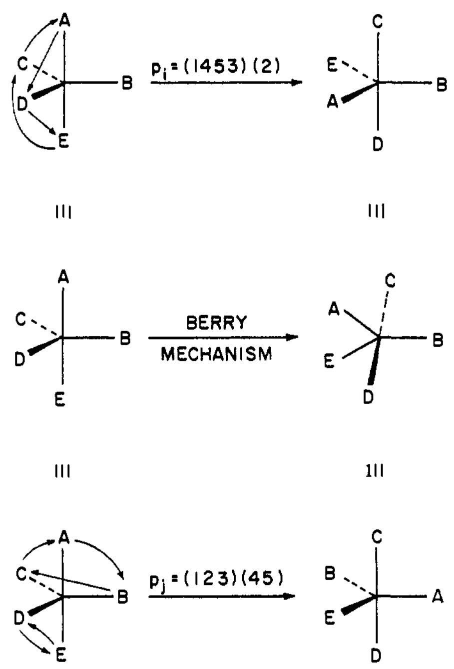

Figure 3. Two permutational isomerization reactions implied by the Berry mechanism. Skeletal positions are labeled as in Figure 1a.

generated by the permutational isomerization reactions p_0 and p_0', respectively. Then T and T' are identical if and only if

$$p_0' = r_p \cdot p_0 \cdot r_q \quad r_p, r_q \epsilon R \tag{2}$$

where R is the permutation group representing rotations, as defined above.

Proof. The directed topological representations T and T' are identical if all the points connected by directed lines in T are also connected by directed lines in T' and *vice versa*. More precisely, T and T' are identical when eq 1 holds if and only if eq 3 holds for all identical pairs $c_i, c_j \epsilon C$ and some $r_k, r_l, r_m, r_n \epsilon R$.

$$p_0' \cdot r_m \cdot c_i = r_n \cdot c_j \tag{3}$$

In the first part of the proof we wish to establish that given eq 1 we can proceed to eq 3 if eq 2 holds. First, eq 2 is rewritten

$$p_0 = r_p^{-1} \cdot p_0' \cdot r_q^{-1} \tag{4}$$

Substituting eq 4 into eq 1

$$r_p^{-1} \cdot p_0' \cdot r_q^{-1} \cdot r_k \cdot c_i = r_l \cdot c_j \tag{5}$$

Operating on both sides of eq 5 with r_p, eq 6 is obtained.

$$p_0' \cdot r_k^{-1} \cdot r_k \cdot c_i = r_p \cdot r_l \cdot c_j \tag{6}$$

Now let $r_m = r_q^{-1} \cdot r_k$ and $r_n = r_p \cdot r_l$, where r_m and r_n are also in the group R. Substituting these into eq 6 we obtain eq 3. The above arguments can of course be used to show that eq 3 and 2 imply eq 1.

To complete the proof we show that if eq 1 and 3 are assumed, then eq 2 must hold true. Letting $r_t = r_l \cdot r_n^{-1}$ and multiplying both sides of eq 3 by r_t, we obtain

$$r_t \cdot p_0' \cdot r_m \cdot c_i = r_l \cdot c_j \tag{7}$$

Equations 1 and 7 may be combined to yield

$$r_t \cdot p_0' \cdot r_m \cdot c_i = p_0 \cdot r_k \cdot c_i \tag{8}$$

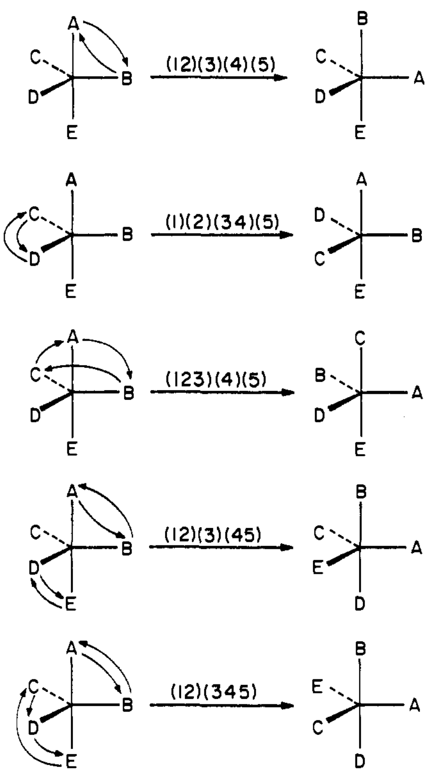

Figure 4. Five *differentiable permutational isomerization reactions* of a D_{3h} molecule in a chiral environment. Skeletal positions are labeled as in Figure 1a.

Equation 8 is now multiplied by r_t^{-1}, c_i^{-1}, and r_m^{-1} in the following manner

$$r_t^{-1} \cdot r_t \cdot p_0' \cdot r_m \cdot c_i \cdot c_i^{-1} \cdot r_m^{-1} = r_t^{-1} \cdot p_0 \cdot r_k \cdot c_i \cdot c_i^{-1} \cdot r_m^{-1} \tag{9}$$

This reduces to

$$p_0' = r_t^{-1} \cdot p_0 \cdot r_k \cdot r_m^{-1} \tag{10}$$

Letting $r_q = r_k . r_m^{-1}$ and $r_p = r_t^{-1}$ in eq 10, we obtain eq 2 and the proof is complete.

Two permutational isomerization reactions p_0 and p_0' are defined as nondifferentiable in a chiral environment if eq 2 holds and as differentiable in a chiral environment if eq 2 does not hold.[6] A number D_R' has been defined as the number of differentiable permutational isomerization reactions in a chiral environment; formulas for calculation of D_R' have been derived.[6] Therefore for any system of permutational isomers, if we produce a set of D_R' permutational isomerization reactions formally differentiable in a chiral environment, we can be assured that any other permutational isomerization reaction will be formally nondifferentiable from one of these D_R' reactions in a chiral environment. An example is shown in Figure 4 for a five-coordinate D_{3h} molecule ($D_{D_3}' = 5$).[6] Once we have drawn the five directed topological representations generated by the reactions shown in Figure 4, we are assured that any other permutation in S_5 will generate a directed topological representation identical with one of those already constructed.

Conventional Topological Representations

For a six-coordinate octahedral molecule, $D_0' = 6$. A set of six permutational isomerization reactions differentiable in a chiral environment is shown in Figure 5. It is disconcerting to our chemical intuition that the permutation (123)(4)(5)(6) and the permutation (132)(4)(5)(6) for the "reverse" reaction are both included in this figure. This situation stems from the definition of directed topological representation since "right-handed" and "left-handed" reactions are formally differentiable in a chiral environment. To circumvent this distinction, we wish to modify our definition such that these reactions are considered one and the same process. This new definition should also be in concord with the conventional definition[4] of topological representations insofar as lines, not directed lines, connect points representing isomers.

Let G be the permutation group representing the full molecular point group G'. Operations in G permute indices of the skeletal positions. In Figure 5, $G' = O_h$. An improper operation in G', namely a reflection operation, transforms the arrows describing $p_i = (123)(4)(5)(6)$ into the arrows describing $p_j = (132)(4)(5)(6)$. Another way of describing this equivalence is $p_j = g_i \cdot p_i \cdot g_i^{-1}$, where $g_i = (1)(23)(4)(56)$.[12] We say that p_j is a "mirror image" of p_i. In general, a "mirror image" of a permutational isomerization reaction p_n is defined as $p_m = g_i \cdot p_n \cdot g_i^{-1}$ where $g_i \epsilon G$ represents an improper operation in G'.[13] We now have sufficient background to define a conventional topological representation.

A *topological representation* is a labeled graph where each labeled point represents a permutational isomer and each line represents a permutational isomerization reaction. Each point is labeled by a coset representative $c_i \epsilon C$. Points c_i and c_j are connected by a line if eq 11 and/or eq 12 hold for some $r_l, r_m, r_n, r_p \epsilon R$. Here,

$$r_l \cdot c_j = w_k \cdot r_m \cdot c_i \tag{11}$$

$$r_n \cdot c_i = w_k \cdot r_p \cdot c_j \tag{12}$$

w_k is either the permutation p_0 or a "mirror image" of p_0. In other words, points representing isomers c_i and c_j are connected by a line if the permutational isomerization reaction p_0 or its "mirror image" converts one isomer into the other.[14]

Using the arguments presented in the theorem of the previous section, it can be shown that the permutations p_0 and p_0' will generate identical topological representations if (a) p_0 and p_0' are formally nondifferentiable in a chiral environment or (b) p_0^{-1} and p_0' are nondifferentiable in a chiral environment or (c) any "mirror image" of p_0' is formally nondifferentiable from p_0 or p_0^{-1} in a chiral environment. This means that there may be less than D_R' different topological representations for a given system of isomers. D_R', however, does place an upper limit on the number of reactions which generate different topological representations.

In Figure 5, (16)(2)(3)(45) is a "mirror image" of (15)(2)(3)(46). Also, (123)(4)(5)(6) and (132)(4)(5)(6) are "mirror images." Consequently there exist only four permutational isomerization reactions which generate different topological representations for the six coordinate octahedral case.

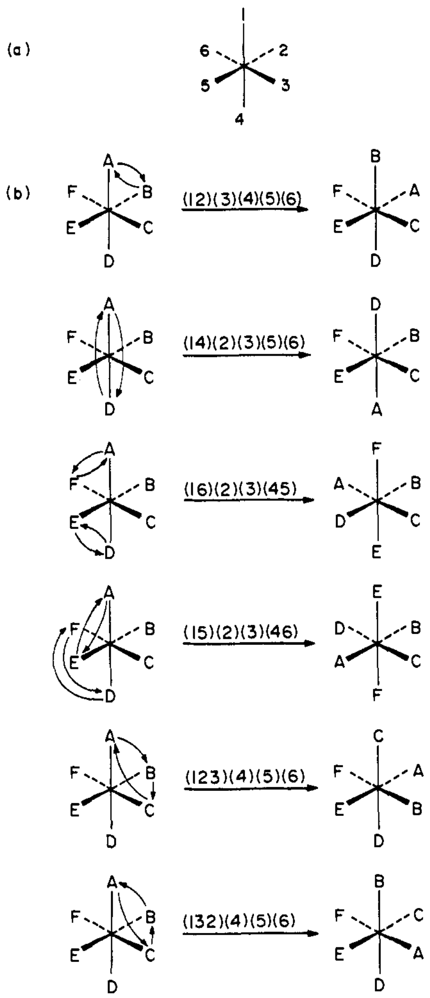

Figure 5. The illustration (a) defines the indexing of positions on an octahedral skeletal framework; (b) lists six *differentiable permutational isomerization reactions* in a chiral environment.

Consulting Figure 4, it is evident that each reaction, its inverse, and its mirror image are formally nondifferentiable in a chiral environment. There exist therefore only five permutational isomerization reactions which generate different topological representations for the five-coordinate trigonal-bipyramidal case.

Conclusions

If a property of chemical compounds undergoing permutational isomerization reactions is defined in terms of a topological representation, the results of this paper may be extended. For example, a stereochemical matrix[4] may be defined in terms of a topological representation. Therefore D_R' places an upper limit on the number of permutational isomerization reactions which generate different stereochemical matrices.

Closure properties[4] may also be defined in terms of topological representations. A system of $n!/|R|$ permutations isomers is said to be closed if all isomers may be interconverted by repeated operation of the permutational isomerization reaction in question. In the

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(12) For discussion of this equivalence relation, see F. A. Cotton, "Chemical Applications of Group Theory," Interscience, New York, N. Y., 1963, p 48.

(13) "Mirror image" is written in quotes because g_i does not necessarily represent a reflection operation in G' but may represent any improper operation in G'.

(14) The present definition of topological representations differs from the conventional definition[4] only in that "mirror images" are not differentiated. The new definition is warranted by its more operational character. Of course the original definition[4] also covers a wider class of isomerization reactions, namely, polytopal rearrangements in general.

topological representation of a closed system, any two points will thus be connectable by a series of lines, *i.e.*, a chain.[4] Such a topological representation is said to be connected. Conversely, connected topological representations represent closed stereochemical systems of permutational isomers. Since nondifferentiable reactions generate identical topological representations, nondifferentiability implies identical closure properties. For example, if p_0 generates a closed stereochemical system and p_0' is not differentiable from p_0 in a chiral environment, then p_0' also generates a closed stereochemical system.

Brocas' kinetic treatment of permutational isomerization reactions[15] is based on topological representations. One can easily show that if two reactions generate the same topological representation, their eigenvectors (as defined by Brocas) must be the same.

The concepts developed in this paper are thus seen to be useful for the description and solution of many problems in dynamic stereochemistry.

Acknowledgments. I am deeply indebted to Dr. Bertram Frenz for his help in revising the manuscript for publication.

(15) J. Brocas, *Theor. Chim. Acta*, **21**, 79 (1971).

On the Mechanism of Reduction of Cobalt(III) and Ruthenium(III) Hexaammine Complexes by Several Aliphatic Radicals

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Abstract: The specific rates of reaction of several aliphatic radicals with $Co(NH_3)_6^{3+}$ and $Ru(NH_3)_6^{3+}$ were determined. Radicals on the α carbon relative to OH or NH_2 groups were shown to be stronger reducing agents than radicals on the α carbon to a carboxylic or an amide group. The reactivity of the radicals $\dot{C}H_2OH$, $CH_3\dot{C}HOH$, $(CH_3)_2\dot{C}OH$, $CH_3\dot{C}OHCOO^-$, and $CH_3CO\dot{C}(O^-)CH_3$, toward $Ru(NH_3)_6^{3+}$ increases along this series, whereas the reversed order of reactivities is found for the reactions with $Co(NH_3)_6^{3+}$ and Cu_{aq}^{2+}. This order is different from the order of reactivities toward nitrobenzene and 2,3-butanedione where the reactivity increases along the series $CH_3\dot{C}OHCO_2^-$, $\dot{C}H_2OH$, $CH_3\dot{C}HOH$, and $(CH_3)_2\dot{C}OH$. The latter order is identical with that of increasing pK of the OH group. The results are interpreted as suggesting that the contribution of π character to the orbital containing the unpaired electron in the radical significantly affects the specific rates of reactions. The implication of the results in radiobiology is discussed.

It has been suggested that aliphatic radicals, usually produced by hydrogen abstraction reactions, are relatively strong reducing agents.[1-4] Such radicals have been shown to reduce different organic compounds[1-3] and metal cations[4,5] both in organic and aqueous media. It has been shown that the specific rate of reduction depends on the structure of the radicals. Radicals α to a hydroxylic or amino group being relatively strong reducing agents whereas radicals α to a carboxylic group were shown to be less reactive. It has been suggested that many of these reduction reactions take place *via* an outer-sphere electron-transfer mechanism.[6]

Organic compounds are often used[7] as hydroxyl radical scavengers when reactions of e_{aq}^- or hydrogen atoms are studied in radiation chemistry.[7] However, relatively little is known on the chemical properties of the radicals formed. This is believed to be of major importance in radiobiological systems, where most of the secondary intermediates are expected to be aliphatic radicals.

The reduction of cobalt(III) and ruthenium(III) hexaammine complexes proceeds always *via* the outer-sphere mechanism.[8] The only exception to this rule, suggested in the literature, is for the reduction of $Co(NH_3)_6^{3+}$ by OH radicals, which was suggested to proceed *via* hydrogen abstraction from the ammine groups.[9] It will be shown that this mechanism does not apply for the radical reactions described in this study. We have decided to measure the specific rates of reduction of the latter complexes by several aliphatic radicals, with the hope of achieving a better understanding of their properties as outer-sphere reducing agents.

Experimental Section

Materials. All solutions were prepared from triple distilled water. Cobalt(III) hexaammine perchlorate was precipitated with perchloric acid from a solution of $[Co(NH_3)_6]Cl_3$, supplied by K & K. The precipitate was purified by two recrystallizations from water. Ruthenium hexaammine chloride from Johnson,

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