The Solution of the Rate Equations for Berry Processes

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The symmetry of the matrix describing the rate equations for Berry intramolecular rearrangements is studied. It is shown that this matrix is invariant with respect to any element of a cyclic group of order ten which has been defined previously [9]. This property is used to obtain the relaxation times, the chemical normal modes and the solution of the rate equations corresponding to Berry processes. Other possible applications are announced.

Die Symmetrie der Matrix für die Kinetik der intramolekularen Berry-Umlagerung wird untersucht. Sie ist invariant gegenüber jedem Element der früher behandelten cyclischen Gruppe 10. Ordnung [9]. Damit lassen sich Relaxationszeiten, chemische Normalmode und die Lösung der zugehörigen kinetischen Gleichungen ermitteln. Auf weitere Anwendungsmöglichkeiten wird außerdem hingewiesen.

On étudie la symétrie de la matrice qui décrit les équations de vitesse pour les réarrangements intramoléculaires de Berry. On montre que cette matrice est invariante pour tout élément d'un groupe cyclique d'ordre dix qui a été défini précédemment [9]. Cette propriété est utilisée pour obtenir les temps de relaxation, les modes normaux chimiques et la solution des équations de vitesse correspondant aux processus de Berry. La possibilité d'autres applications est annoncée.

Introduction

It is well-known that five coordinate complexes may undergo various intramolecular rearrangements [1]. Of these, the Berry [2] mechanism seems to provide a good description of the isomerization of these molecules, as long as the five ligands are not too different in size. The Berry mechanism has been studied by numerous authors who have discussed the main features of its topological [3–6] and matrix [7, 8] representations. More recently, group generators associated to isomerizations of five coordinate complexes have also been defined [9]. In this paper we use these generators in order to derive some new properties of both topological and matrix representations. As a consequence, we obtain the explicit solution of the rate equations corresponding to Berry processes.

Rate Equations

We consider five coordinate complexes ML_5 where the five ligands L are identical but distinguishable by labelling from 1 to 5. We assume that the ligands are at the vertices of a trigonal bipyramid. Under these conditions, there are twenty isomers which will be numbered according to the convention of Muetterties [1] i.e. 12, 13, 14, 15, 23, 24, 25, 34, 35, 45 and their enantiomers denoted by $\overline{12}$, etc ...

For the moment, we assume that the only mechanism of intramolecular rearrangement is the Berry pseudo-rotation. This process may be visualized as the simultaneous motion of two equatorial ligands to apical positions and of the two apical ligands to equatorial ones. The third equatorial ligand — the pivot — remains fixed. As we have three possible choices for the pivot, three different isomers may be reached from a given one. This pseudo-rotation proceeds through a transition state of tetragonal pyramidal form.

The time evolution of the concentrations C_i (of isomer i) is governed by the set of twenty coupled differential equations:

$$\frac{d C_i}{d t} = \kappa(C_n + C_l + C_m) - 3\kappa C_i,\tag{1}$$

where C_n, C_l and C_m represent the concentrations of the three isomers which may be reached from i in one Berry step. In our simplified description, the rate constant κ is the same for each Berry step. This is consistent with the approximation that the five ligands are identical which implies that the isolated molecule is characterized by two energies: one for the trigonal bipyramids and one for the tetragonal pyramids (transition state).

To write down explicitly the set of differential Eqs. (1), one may use the topological graphs which have been elaborated previously for Berry pseudo-rotation [3–6]. For example, Fig. 1 shows a three-dimensional graph proposed by Gielen and Nasielski.

An alternative way of representing the isomerizations is provided by matrix formulation. This type of representation has already been described in the literature [7, 8] and it may of course be used as a compact way of writing the set of Eqs. (1). To make it more precise, let us introduce some notations[1].

The composition of the system is characterized by twenty concentrations. Thus, a vector space of dimension twenty i" needed for its mathematical description. The basis of the representation consists of twenty orthonormal column vectors $e_i (1 \leq i \leq 20)$ with twenty rows. Each row of e_i is zero except the row i
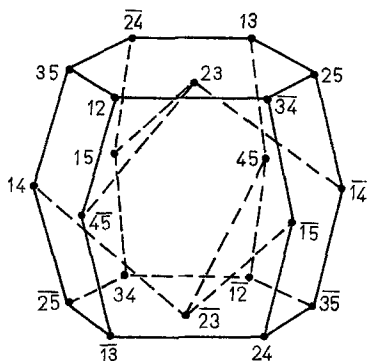

Fig. 1. A graph for Berry steps

[1] Details about matrix formulation in chemical kinetics may be found in many textbooks [10].

which is the unity. The composition vector C will be written:

$$C = \sum_{i=1}^{20} C_i e_i \tag{2}$$

and is also a column vector. We choose to associate the values $1, 2, \ldots 20$ of index i respectively to the isomers.

$$12, 34, \overline{13}, 25, \overline{35}, 14, 45, 23, \overline{24}, \overline{15}, \overline{12}, \overline{34}, 13, \overline{25}, 35, \overline{14}, \overline{45}, \overline{23}, 24, 15 . \tag{3}$$

The reason for this choice will become clear in the following.

In this notation, the set (1) reads:

$$\frac{dC}{dt} = \kappa[A - 3E] \cdot C , \tag{4}$$

where E is the unit matrix of dimension twenty and the matrix A is, apart from the order of the rows and columns, the same as the matrix for Berry pseudo-rotation which is found in the literature [8], i. e.:

$$A = \begin{bmatrix}
. & . & . & . & . & . & . & . & . & . & a_1 & . & . & b_1 & . & b_4' & . & . & . \\
. & . & . & . & . & . & . & . & . & a_6' & . & . & c_1 & . & . & . & . & . & c_{10}' \\
. & . & . & . & . & . & . & . & . & . & . & a_7 & . & . & b_7 & . & b_{10}' & . \\
. & . & . & . & . & . & . & . & . & c_6' & a_2 & . & . & c_7 & . & . & . & . \\
. & . & . & . & . & . & . & . & b_6' & . & . & . & . & a_3 & . & . & b_3 & . \\
. & . & . & . & . & . & . & . & . & c_2' & a_8 & . & . & c_3 & . & . \\
. & . & . & . & . & . & . & . & b_9 & . & b_2' & . & . & . & . & a_9 & . & . \\
. & . & . & . & . & . & . & . & . & . & . & c_8' & a_4' & . & . & . & c_9 \\
. & . & . & . & . & . & . & . & b_5 & . & b_8' & . & . & . & . & . & a_5 \\
. & . & . & . & . & . & . & . & c_5 & . & . & . & . & . & . & c_4' & a_{10}' & . \\
. & a_6 & . & . & b_6 & . & b_9' & . & . & . & . & . & . & . & . & . & . \\
a_1' & . & . & c_6 & . & . & . & . & c_5' & . & . & . & . & . & . & . \\
. & . & . & a_2 & . & . & b_2 & . & b_5' & . & . & . & . & . & . \\
. & c_1' & a_7' & . & . & c_2 & . & . & . & . & . & . & . & . \\
b_1' & . & . & . & . & a_8 & . & . & b_8 & . & . & . & . & . \\
. & . & . & . & c_7' & a_3' & . & . & c_8 & . & . & . & . \\
b_4 & . & b_7' & . & . & . & . & a_4 & . & . & . & . & . \\
. & . & . & . & . & c_3' & a_9' & . & . & c_4 & . \\
. & . & b_{10} & . & b_3' & . & . & . & . & a_{10} & . \\
. & c_{10} & . & . & . & . & . & c_9' & a_5' & . & . \\
\end{bmatrix} \tag{5}$$

where the constants $a_p, b_p, c_p, a_p', b_p', c_p'$ $(1 \leqq p \leqq 10)$ have to be put equal to one. For the moment, we use different symbols for further reference.

We are now in a position to study the symmetry properties of matrix A and to use them to solve the rate Eqs. (1). This program will be accomplished in the next sections.

Symmetry of the Matrix A

In a previous paper [9], the relation between stereoisomerism of five-coordinate complexes and the cyclic group of order ten has been stressed. Let us study the symmetry of the matrix A in connection with the generators Q and I of this group, defined in the following way. The operator I is the geometrical inversion about the centre of the trigonal bipyramid. It transforms any isomer into its enantiomer. The operator Q is a cyclic permutation of order five on the five ligands. Let us choose $Q = (13542)$ where the symbol $(d_1 d_2 \dots d_n)$ represents the operation of replacing each letter in the symbol by the one which follows it[2]. The powers of Q are readily calculated [11]: $Q^2 = (15234)$, $Q^3 = (14325)$, $Q^4 = (12453)$, $Q^5 = 1$. The operators Q and I commute and their product $R = QI$ is a generator for the cyclic group of order ten: this group contains the ten elements $S = R^p (1 \leqq p \leqq 10)$.

Let us examine the chemical significance of these operators. Acting on isomer 12, the powers of Q give respectively $\overline{13}, \overline{35}, 45, \overline{24}$ and the action of I generates the five corresponding enantiomers. In the same way, the action of Q and its powers on one of the isomers which has not yet been touched, say 34, gives $25, 14, 23, \overline{15}$. It is seen that Q divides the isomers in four families I, $\overline{\text{I}}$, II and $\overline{\text{II}}$. Family I contains the isomers $12, \overline{13}, \overline{35}, 45, \overline{24}$, II contains $34, 25, 14, 23$ and $\overline{15}$; $\overline{\text{I}}$ and $\overline{\text{II}}$ denote the families of the enantiomers of families I and II[3].

It is easy to draw the matrix R corresponding to the generator R: we have only to calculate, for each i,

$$R\,e_i = e_{R(i)}, \tag{6}$$

where $R(i)$ is the index of the isomer generated by R starting from the isomer of index i. For example, if $i = 1$ (isomer 12), $R(i)$ corresponds to isomer 13. The matrix elements R_{ji} are then obtained by performing the scalar products $e_j \cdot R e_i$. One gets:

$$R_{ji} = e_j \cdot R e_i = e_j \cdot e_{R(i)} = \delta_{j, R(i)} \tag{7}$$

because of the orthonormality of the vectors e_i. In Eq. (7) we used the Kronecker δ_{ji} symbol which is one if $j = i$ and zero otherwise. The explicit form of matrix R is given below.

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[2] For convenience, this Q is not the permutation used earlier [9] but the structure of the two groups is of course the same.

[3] It must be noted that the same permutation Q may perform different chemical operations. In this case Q is the twist of one apical and two equatorial ligands for family I but for family II it corresponds to a process which gives the enantiomer of a Berry step (respectively processes 4 and 5 described earlier [1]).

$$R = \begin{bmatrix}
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot
\end{bmatrix} \qquad (8)$$

It is necessary now to study the relation between A and R. To do this we calculate $R^{-1}AR = B$. Using Eq. (7), one gets for B_{ij}:

$$B_{ij} = \sum_{k,l=1}^{20} (R^{-1})_{ik} A_{kl} R_{lj} = \sum_{k,l=1}^{20} \delta_{i,\,R^{-1}(k)} A_{kl} \delta_{l,\,R(j)} = \sum_{k,l=1}^{20} \delta_{k,\,R(i)} A_{kl} \delta_{l,\,R(j)} = A_{R(i),R(j)}.$$

This means that the transform B of A is obtained by performing the operation R on the subscripts of A.

If we examine the matrix A (see Eq. (5)), we remark that $A_{R(i),R(j)} = A_{ij}$ if $a_p = a'_p = b_p = b'_p = c_p = c'_p = 1$. In fact, $A_{S(i),S(j)} = A_{ij}$ if S is any element $R^p (1 \le p \le 10)$ of the cyclic group. This is illustrated in Eq. (5) where the effect of R on the matrix elements of A transforms a_1 successively into $a_2, \dots a_k \dots a_{10}$. The same is true starting from a'_1, b_1, b'_1, c_1 and c'_1. Since all these symbols must be put equal to one, we have indeed:

$$S^{-1}AS = A$$

which means that the matrix for Berry processes is invariant with respect to any element S of the cyclic group of order 10. This is easy to verify explicitly from Eqs. (5) and (8).

Eigenvalues and Eigenfunctions

This result may be used for diagonalizing the matrix A because of a theorem of group theory which may be stated as follows: if a matrix (here A) is invariant under any element of a group (here the cyclic group of order ten), then the matrix is block-diagonal in the irreducible representations of the group. The dimension of the block corresponding to a given irreducible representation M is at most

the product of the dimension of this representation by the number of times g_M it occurs in the considered reducible representation of the group[4].

The irreducible representations of the group are, in our case, one-dimensional because the group is commutative. If we want to diagonalize R, we need its twenty eigenvectors $\Phi_j (1 \leqq j \leqq 20)$:

$$R \cdot \Phi_j = \lambda_j \Phi_j. \tag{9}$$

It is easy to verify that each column of the matrix M,

$$M = \left(\frac{1}{10}\right)^{\frac{1}{2}} \begin{bmatrix}
1 & . & 1 & . & 1 & . & 1 & . & 1 & . & 1 & . & 1 & . & 1 & . & 1 & . & 1 & . \\
. & 1 & . & 1 & . & 1 & . & 1 & . & 1 & . & 1 & . & 1 & . & 1 & . & 1 & . & 1 \\
1 & . & 1 & . & \varepsilon & . & \varepsilon & . & \varepsilon^2 & . & \varepsilon^2 & . & \varepsilon^3 & . & \varepsilon^3 & . & \varepsilon^4 & . & \varepsilon^4 & . \\
. & 1 & . & 1 & . & \varepsilon & . & \varepsilon & . & \varepsilon^2 & . & \varepsilon^2 & . & \varepsilon^3 & . & \varepsilon^3 & . & \varepsilon^4 & . & \varepsilon^4 \\
1 & . & 1 & . & \varepsilon^2 & . & \varepsilon^2 & . & \varepsilon^4 & . & \varepsilon^4 & . & \varepsilon & . & \varepsilon & . & \varepsilon^3 & . & \varepsilon^3 & . \\
. & 1 & . & 1 & . & \varepsilon^2 & . & \varepsilon^2 & . & \varepsilon^4 & . & \varepsilon^4 & . & \varepsilon & . & \varepsilon & . & \varepsilon^3 & . & \varepsilon^3 \\
1 & . & 1 & . & \varepsilon^3 & . & \varepsilon^3 & . & \varepsilon & . & \varepsilon & . & \varepsilon^4 & . & \varepsilon^4 & . & \varepsilon^2 & . & \varepsilon^2 & . \\
. & 1 & . & 1 & . & \varepsilon^3 & . & \varepsilon^3 & . & \varepsilon & . & \varepsilon & . & \varepsilon^4 & . & \varepsilon^4 & . & \varepsilon^2 & . & \varepsilon^2 \\
1 & . & 1 & . & \varepsilon^4 & . & \varepsilon^4 & . & \varepsilon^3 & . & \varepsilon^3 & . & \varepsilon^2 & . & \varepsilon^2 & . & \varepsilon & . & \varepsilon & . \\
. & 1 & . & 1 & . & \varepsilon^4 & . & \varepsilon^4 & . & \varepsilon^3 & . & \varepsilon^3 & . & \varepsilon^2 & . & \varepsilon^2 & . & \varepsilon & . & \varepsilon \\
1 & . & -1 & . & 1 & . & -1 & . & 1 & . & -1 & . & 1 & . & -1 & . & 1 & . & -1 & . \\
. & 1 & . & -1 & . & 1 & . & -1 & . & 1 & . & -1 & . & 1 & . & -1 & . & 1 & . & -1 \\
1 & . & -1 & . & \varepsilon & . & -\varepsilon & . & \varepsilon^2 & . & -\varepsilon^2 & . & \varepsilon^3 & . & -\varepsilon^3 & . & \varepsilon^4 & . & -\varepsilon^4 & . \\
. & 1 & . & -1 & . & \varepsilon & . & -\varepsilon & . & \varepsilon^2 & . & -\varepsilon^2 & . & \varepsilon^3 & . & -\varepsilon^3 & . & \varepsilon^4 & . & -\varepsilon^4 \\
1 & . & -1 & . & \varepsilon^2 & . & -\varepsilon^2 & . & \varepsilon^4 & . & -\varepsilon^4 & . & \varepsilon & . & -\varepsilon & . & \varepsilon^3 & . & -\varepsilon^3 & . \\
. & 1 & . & -1 & . & \varepsilon^2 & . & -\varepsilon^2 & . & \varepsilon^4 & . & -\varepsilon^4 & . & \varepsilon & . & -\varepsilon & . & \varepsilon^3 & . & -\varepsilon^3 \\
1 & . & -1 & . & \varepsilon^3 & . & -\varepsilon^3 & . & \varepsilon & . & -\varepsilon & . & \varepsilon^4 & . & -\varepsilon^4 & . & \varepsilon^2 & . & -\varepsilon^2 & . \\
. & 1 & . & -1 & . & \varepsilon^3 & . & -\varepsilon^3 & . & \varepsilon & . & -\varepsilon & . & \varepsilon^4 & . & -\varepsilon^4 & . & \varepsilon^2 & . & -\varepsilon^2 \\
1 & . & -1 & . & \varepsilon^4 & . & -\varepsilon^4 & . & \varepsilon^3 & . & -\varepsilon^3 & . & \varepsilon^2 & . & -\varepsilon^2 & . & \varepsilon & . & -\varepsilon & . \\
. & 1 & . & -1 & . & \varepsilon^4 & . & -\varepsilon^4 & . & \varepsilon^3 & . & -\varepsilon^3 & . & \varepsilon^2 & . & -\varepsilon^2 & . & \varepsilon & . & -\varepsilon
\end{bmatrix} \tag{10}$$

where $\varepsilon = e^{i\frac{2\pi}{5}}$, is an eigenvector of R. Moreover, the eigenvectors are orthogonal to each other and have been normalized by the factor $(1/10)^{\frac{1}{2}}$. Therefore, M is unitary, and its inverse M^{-1} is merely its adjoint. The product $\tilde{R} = M^{-1} \cdot R \cdot M$ is readily calculated. Of course $\tilde{R}$ is diagonal and its eigenvalues are respectively:

$$1, 1, -1, -1, \varepsilon^4, \varepsilon^4, -\varepsilon^4, -\varepsilon^4, \varepsilon^3, \varepsilon^3, -\varepsilon^3, -\varepsilon^3, \varepsilon^2, \varepsilon^2, -\varepsilon^2, -\varepsilon^2, \varepsilon, \varepsilon, -\varepsilon, -\varepsilon. \tag{11}$$

It is seen that each eigenvalue appears twice. This arises from the fact that the twenty dimensional matrix R contains twice each of the ten one-dimensional irreducible representations of the cyclic group of order ten (once for families I and $\bar{\text{I}}$, once for families II and $\bar{\text{II}}$). Hence, if we had constructed the ten matrices S of dimension twenty we would have obtained a reducible representation of the cyclic group of order ten where each of the ten one-dimensional irreducible

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[4] This procedure is analogous to normal-mode analysis in molecular vibrations [12]. Details and demonstrations of the results which are cited here can be found elsewhere [13, 14].

representations would have occurred twice. From this we conclude that in the representation (9) the matrix A is block diagonal and that each block is of dimension two. In other words, the matrix

$$\tilde{A} = M^{-1} \cdot A \cdot M \tag{12}$$

has ten blocks of dimension two along its main diagonal.

The matrix $\tilde{A}$ may indeed be calculated explicitly from Eqs. (5) and (10). Its ten blocks are respectively:

$$\begin{pmatrix} 2 & 1 \\ 1 & 2 \end{pmatrix}, \begin{pmatrix} -2 & -1 \\ -1 & -2 \end{pmatrix}, \begin{pmatrix} \alpha & 1 \\ 1 & \beta \end{pmatrix}, \begin{pmatrix} -\alpha & -1 \\ -1 & -\beta \end{pmatrix}, \begin{pmatrix} \beta & 1 \\ 1 & \alpha \end{pmatrix}, \begin{pmatrix} -\beta & -1 \\ -1 & -\alpha \end{pmatrix}, \begin{pmatrix} \beta & 1 \\ 1 & \alpha \end{pmatrix}, \begin{pmatrix} -\beta & -1 \\ -1 & -\alpha \end{pmatrix},$$

$$\begin{pmatrix} \alpha & 1 \\ 1 & \beta \end{pmatrix}, \begin{pmatrix} -\alpha & -1 \\ -1 & -\beta \end{pmatrix} \tag{13}$$

where one has:

$$\alpha = \varepsilon^2 + \varepsilon^3 = \frac{-1 - \sqrt{5}}{2}$$

$$\beta = \varepsilon + \varepsilon^4 = \frac{-1 + \sqrt{5}}{2}. \tag{14}$$

It is now an easy matter to obtain the eigenvalues and the eigenfunctions of A from the eigenvalues and eigenfunctions of the blocks (13): the first block has the eigenvalues 1 and 3 and the third block gives -2 and again 1. The eigenvalues of the other blocks are the same or differ merely by their sign. Because

$\psi_1 = \dfrac{1}{\sqrt{2}} \{\Phi_1 + \Phi_2\}$	3	$\psi_2 = \dfrac{1}{\sqrt{2}} \{\Phi_1 - \Phi_2\}$	1	
$\psi_3 = \dfrac{1}{\sqrt{2}} \{\Phi_3 + \Phi_4\}$	-3	$\psi_4 = \dfrac{1}{\sqrt{2}} \{\Phi_3 - \Phi_4\}$	-1	
$\psi_5 = \dfrac{1}{\sqrt{3(1-\alpha)}} \{\Phi_5 + (1-\alpha)\,\Phi_6\}$	1	$\psi_6 = \dfrac{1}{\sqrt{3(2+\alpha)}} \{\Phi_5 - (2+\alpha)\,\Phi_6\}$	-2	
$\psi_7 = \dfrac{1}{\sqrt{3(1-\alpha)}} \{\Phi_7 + (1-\alpha)\,\Phi_8\}$	-1	$\psi_8 = \dfrac{1}{\sqrt{3(2+\alpha)}} \{\Phi_7 - (2+\alpha)\,\Phi_8\}$	2	
$\psi_9 = \dfrac{1}{\sqrt{3(2+\alpha)}} \{\Phi_9 + (2+\alpha)\,\Phi_{10}\}$	1	$\psi_{10} = \dfrac{1}{\sqrt{3(1-\alpha)}} \{\Phi_9 - (1-\alpha)\,\Phi_{10}\}$	-2	
$\psi_{11} = \dfrac{1}{\sqrt{3(2+\alpha)}} \{\Phi_{11} + (2+\alpha)\,\Phi_{12}\}$	-1	$\psi_{12} = \dfrac{1}{\sqrt{3(1-\alpha)}} \{\Phi_{11} - (1-\alpha)\,\Phi_{12}\}$	2	
$\psi_{13} = \dfrac{1}{\sqrt{3(2+\alpha)}} \{\Phi_{13} + (2+\alpha)\,\Phi_{14}\}$	1	$\psi_{14} = \dfrac{1}{\sqrt{3(1-\alpha)}} \{\Phi_{13} - (1-\alpha)\,\Phi_{14}\}$	-2	
$\psi_{15} = \dfrac{1}{\sqrt{3(2+\alpha)}} \{\Phi_{15} + (2+\alpha)\,\Phi_{16}\}$	-1	$\psi_{16} = \dfrac{1}{\sqrt{3(1-\alpha)}} \{\Phi_{15} - (1-\alpha)\,\Phi_{16}\}$	2	
$\psi_{17} = \dfrac{1}{\sqrt{3(1-\alpha)}} \{\Phi_{17} + (1-\alpha)\,\Phi_{18}\}$	1	$\psi_{18} = \dfrac{1}{\sqrt{3(2+\alpha)}} \{\Phi_{17} - (2+\alpha)\,\Phi_{18}\}$	-2	
$\psi_{19} = \dfrac{1}{\sqrt{3(1-\alpha)}} \{\Phi_{19} + (1-\alpha)\,\Phi_{20}\}$	-1	$\psi_{20} = \dfrac{1}{\sqrt{3(2+\alpha)}} \{\Phi_{19} - (2+\alpha)\,\Phi_{20}\}$	2	

of the structure of $\tilde{A}$, see (13), the eigenfunctions of A will each be a linear combination of two consecutive columns Φ_j of M. They mix a vector of one subspace (families $I + \bar{I}$) with a vector of the other subspace (families $II + \bar{II}$). The explicit form of the twenty normalized eigenvectors ψ_s and the corresponding eigenvalues of A are given in the next table where the vectors belonging to the same irreducible representation of the cyclic group of order ten have been written on the same line.

Time Evolution

Let us now construct the matrix N whose twenty columns are the eigenvectors ψ_s with their index s in the natural order. By definition of γ, we write:

$$N^{-1} C = \gamma , \tag{15}$$

where N^{-1} is again equal to the adjoint of N because N is unitary. Multiplying (4) from the left by N^{-1}, we get:

$$\frac{d\gamma}{dt} = \kappa N^{-1} [A - 3E] N \gamma , \tag{16}$$

where the matrix $N^{-1} [A - 3E] N = H$ is now a diagonal matrix whose elements h_s are obtained from the eigenvalues of A by subtracting a term 3. The result is given below.

Value of S	1	8, 12, 16, 20	2, 5, 9, 13, 17	4, 7, 11, 15, 19	6, 10, 14, 18	3
Value of h_s	0	-1	-2	-4	-5	-6
Degeneracy	1	4	5	5	4	1

As it is expected, the eigenvalues are real and non positive [15].

Because of the diagonal form of H, the system of twenty coupled Eqs. (1) is now replaced by twenty uncoupled differential equations

$$\frac{d\gamma_s}{dt} = \kappa h_s \gamma_s \tag{17}$$

whose solution is

$$\gamma_s = \gamma_s^0 e^{\kappa h_s t} \tag{18}$$

and where γ_s^0 is the value of γ_s at $t = 0$. The Eqs. (17) and (18) are the separate equations for the evolution of the chemical "normal-modes" γ_s corresponding to Berry processes. The explicit form of a "normal-mode" γ_s is obtained from (15) by performing the scalar product of the s-th line of N^{-1}, i. e. the row vector whose elements are the complex conjugate of ψ_s, by the column vector C of (2). Some complex coefficients appear in this operation, which have no physical meaning. As usually, they may be eliminated by noting that any linear combination of eigenvectors with the same eigenvalue is also an eigenvector. For example, the four complex eigenvectors $\psi_6, \psi_{10}, \psi_{14}, \psi_{18}$ belonging to the eigenvalue $h_s = -5$ may be replaced by $\psi_6 + \psi_{18}, \psi_{10} + \psi_{14}, i(\psi_6 - \psi_{18}), i(\psi_{10} - \psi_{14})$ which give normal modes with only real coefficients.

The first normal mode γ_1 is the sum of the twenty concentrations which evolves with zero relaxation time because of the required conservation of the total mass of the system.

We write now the Eq. (18) in matrix form:

$$\gamma = O(t)\,\gamma^0 \,,$$

where $O(t)$ is a diagonal matrix whose elements are $e^{\kappa h_s t}$. By multiplying by N, one gets:

$$C = P(t)\,C^0 \,, \tag{19}$$

where one has put

$$P(t) = N\,O(t)\,N^{-1} \,. \tag{20}$$

These two last equations give the explicit solution of the kinetic equations in the approximation we have considered: the knowledge of the matrix $P(t)$ makes it possible to deduce the concentration of any isomer at time t from the concentrations of all of them at time zero.

Of course, the matrix $P(t)$ may be calculated through (20) because N and $O(t)$ are known explicitly. In this calculation, a simplification occurs: the fact that each isomer plays the same role allows us to evaluate only the first row $p_{1k}(t)$ of $P(t)$ which gives the concentration $C_1(t)$ of isomer 12 as a function of the concentrations of all the isomers at time zero:

$$C_1(t) = \sum_{k=1}^{20} P_{1k}(t)\,C_k^0 \,, \tag{21}$$

where k refers to isomers in the way indicated by (3). If one wants $C_i(t)$ with i corresponding e. g. to isomer (13), one has not to change the values of the P_{ik} but merely to associate to k other isomers than those given by (3) (see Fig. 1).

Even with this simplification, the calculation of P_{1k} remains lengthy and we only give the results. In the following equations, the indices 1 and k have been replaced explicitly by isomer names (between brackets).

$$
\begin{aligned}
C_{(12)}(t) = {}& P_a(t)\,C^0_{(12)} + P_b(t)\,[C^0_{(34)} + C^0_{(35)} + C^0_{(45)}] + P_c(t)\,[C^0_{(13)} + C^0_{(23)} + C^0_{(14)} \\
& + C^0_{(24)} + C^0_{(15)} + C^0_{(25)}] + P_d(t)\,[C^0_{(\overline{13})} + C^0_{(\overline{23})} + C^0_{(\overline{14})} + C^0_{(\overline{24})} + C^0_{(\overline{15})} + C^0_{(\overline{25})}] \\
& + P_e(t)\,[C^0_{(\overline{34})} + C^0_{(\overline{35})} + C^0_{(\overline{45})}] + P_f(t)\,C^0_{(\overline{12})}
\end{aligned} \tag{22}
$$

where:

$$P_a(t) = \frac{1}{20}\,(1 + 4e^{-\kappa t} + 5e^{-2\kappa t} + 5e^{-4\kappa t} + 4e^{-5\kappa t} + e^{-6\kappa t})$$

$$P_b(t) = \frac{1}{60}\,(3 + 8e^{-\kappa t} + 5e^{-2\kappa t} - 5e^{-4\kappa t} - 8e^{-5\kappa t} - 3e^{-6\kappa t})$$

$$P_c(t) = \frac{1}{60}\,(3 + 2e^{-\kappa t} - 5e^{-2\kappa t} - 5e^{-4\kappa t} + 2e^{-5\kappa t} + 3e^{-6\kappa t})$$

$$P_d(t) = \frac{1}{60}\,(3 - 2e^{-\kappa t} - 5e^{-2\kappa t} + 5e^{-4\kappa t} + 2e^{-5\kappa t} - 3e^{-6\kappa t})$$

$$P_e(t) = \frac{1}{60}\,(3 - 8e^{-\kappa t} + 5e^{-2\kappa t} + 5e^{-4\kappa t} - 8e^{-5\kappa t} + 3e^{-6\kappa t})$$

$$P_f(t) = \frac{1}{20}\,(1 - 4e^{-\kappa t} + 5e^{-2\kappa t} - 5e^{-4\kappa t} + 4e^{-5\kappa t} - e^{-6\kappa t}) \,.$$

(23)

In these equations, one has put:

$$P_a(t) = P_{(12)(12)}$$

$$P_b(t) = P_{(12)(\overline{34})} = P_{(12)(35)} = P_{(12)(\overline{45})} \tag{24}$$

$$P_c(t) = P_{(12)(\overline{13})} = P_{(12)(23)} = P_{(12)(14)} = P_{(12)(\overline{24})} = P_{(12)(\overline{15})} = P_{(12)(25)}$$

and similar relations for P_d, P_e, P_f (the isomer of the second parenthese is replaced by its enantiomer). The coefficients $P_a, P_b \ldots P_f$ indicate how the concentration of isomer (12) at time t depends on the initial concentration of the isomers which may be reached from (12) through 0, 1, 2, 3, 4, 5 Berry steps respectively. The equalities (24) express the fact that this kinetic scheme does not distinguish the isomers which may be reached from a given one in the same (minimum) number of steps. This is also the reason why there are six relaxation times.

The expressions (23) must satisfy the two following tests: a) for $t = 0$ $P_a(t)$ should be 1 and the other should be zero and b) since the system is in equilibrium when all the concentrations are the same one should have $P_a(t) + P_f(t) + 3(P_b(t) + P_e(t)) + 6(P_c(t) + P_d(t)) = 1$ for arbitrary t. These conditions are readily verified explicitly.

Conclusion

It is clear that this method could also be applied to stereoisomerization of six coordinate complexes (for example the Bailar twist [16]) and also to the other stereoisomerization of five coordinate complexes [1]. In the latter case, it is expected that the matrix A should have the same eigenvectors as in the Berry case but this remains still to be demonstrated.

In general, the approach we have developped may be useful each time one has to treat chemical kinetics corresponding to polytopal rearrangements [1]. Indeed in this case, one has numerous isomers of the same geometrical form and therefore the matrix describing the kinetic scheme is again expected to have an high symmetry, at least in the approximation of identical ligands distinguishable by labelling. If this approximation is not valid then one has to introduce different rate constants for the different Berry steps and to treat them by perturbation techniques. Since one knows the invariance properties of the unperturbed matrix, the problem must be easy to solve in the present framework and will be initiated in a forthcoming work.

References

1. Muetterties, E. L.: J. Amer. chem. Soc. **91**, 1636 (1969).
2. Berry, S.: J. chem. Physics **32**, 923 (1960).
3. Balaban, A. T., Farcasiu, D., Banica, R.: Rev. Roum. Chim. **11**, 1205 (1966).
4. Dunitz, J. D., Prelog, V.: Angew. Chem. (Int. Ed.) **7**, 726 (1968).
5. Lauterbur, P. C., Ramirez, F.: J. Amer. chem. Soc. **90**, 6722 (1968).
6. Gielen, M., Nasielski, J.: Bull. Soc. chim. Belges **78**, 339 (1969).

7. Muetterties, E. L., Wright, C. M.: Quart. Rev. **21**, 179 (1967).
8. Gielen, M., De Clercq, M., Nasielski, J.: J. Organometal. Chem. **18**, 217 (1969).
9. Brocas, J., Gielen, M.: Bull. Soc. chim. Belges. To be published.
10. See e. g. Eigen, M., de Mayer, L.: In: Technique of organic chemistry, ed. by A. Weissberger. Vol. VIII, Part II.
11. See e. g. Carmichael, R. D.: Introduction to the theory of finite groups. Dover 1956.
12. Wilson, E. B., Decius, J. C., Cross, P. C.: Molecular vibrations. McGraw Hill 1955.
13. Orban, J.: Ph. D. Thesis, Université Libre de Bruxelles, 1969.
14. Ree, F. H., Chesnut, D. A.: J. chem. Physics **45**, 3983 (1966).
15. Prigogine, I.: Etude thermodynamique des phénomènes irréversibles, ed. by Desoer – Liège 1947.
16. Bailar, J. C., Jr.: J. inorg. nuclear Chem. **8**, 165 (1958).

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