numerical values of measured reactant and product concentrations during a MeMA BZ oscillator run are given. Since MeMA is in excess (0.28 M) compared to BrO_3^- ions (0.10 M), the stoichiometry of process 3 requires that 0.11 M MeMA should be left as deuterated or undeuterated species. This is exactly the result found in our experiment (Table I). Finally, we calculate the concentrations of BrMeMA and acetic acid. From the reacting MeMA (0.17 M), 0.10 M BrMeMA and 0.07 M CH_3COOH should be found, when it is assumed that all bromate has reacted. Our observed values for BrMeMA and acetic acid are 0.09 and 0.06 M, respectively (see Table I), which are in fair agreement with the stoichiometric requirement of process 3.

Conclusion

Besides carbon dioxide and traces of formic acid and carbon monoxide the main end products in the Ce(IV)-catalyzed MeMA BZ reaction are BrMeMA and acetic acid. The stoichiometry of reactants and the products which quantitatively have been followed by NMR are found to be in agreement with process 3, showing that the analysis the FKN mechanism was based upon appears to be transferable to the classical MeMA BZ reaction.

It seems an interesting task to look for the kinetic reason why the malonic acid system, in contrast to the MeMA oscillator reported here, has a different net reaction compared with FKN's original proposal.[4] This will be the subject of a comparative kinetic study between malonic acid and MeMA systems using the NMR technique.

Imposition of Geometrical Constraints on Potential Energy Surface Walking Procedures

Hugh Taylor and Jack Simons*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112 (Received: September 21, 1984)

Explicit working expressions are provided for use in applying geometrical constraints to multidimensional potential energy surface walking algorithms. In particular, constraints involving center-of-mass displacements, infinitesimal rotations, planes of symmetry, bond lengths, bond angles, substituent-group internal rotations, and dihedral angles are all treated. The application of such constraints to the Newton–Raphson or Fletcher surface walking procedures, both of which utilize local gradient and curvature data, results in a set of linear algebraic equations to be solved for the Lagrange multipliers associated with the various constraints. The solution of these equations, together with the solution of the Newton–Raphson or Fletcher equations, then allows the computation of a surface walking step which will display the desired behavior as enforced in the constraints. Such automatically enforced constraints are likely to be of most use when dealing with multidimensional systems describing molecules with several low-frequency internal vibrational motions such as group rotations, ring deformations, and pseudorotations.

I. Introduction

Surface walking algorithms which use local gradient and curvature information are routinely used[1] for locating minima and saddle points and for otherwise exploring Born–Oppenheimer potential energy surfaces. Optimizations over relatively few degrees of freedom, both on very small systems and over selected degrees of freedom of larger systems, are typically carried out in terms of internal molecular coordinates.[2] Internal coordinates are convenient in that any "uninteresting" degrees of freedom are automatically constrained by omission. In addition to reducing the dimensionality of the surface to be characterized, such coordinate systems enjoy the advantage that center-of-mass (COM) translations and rotations, which correspond to null eigenvectors for the Hessian matrix, are automatically eliminated from the problem.

Ab initio gradients and Hessians, however, are almost always generated, using quantum chemical computer codes,[3] in terms of the $3N$ space-fixed Cartesian coordinates of all of the N atoms. If such space-fixed coordinates are to be used, COM translations and rotations must somehow be removed from the problem; otherwise, the surface walking algorithms mentioned above will generate undesirable overall displacements of the molecule corresponding to translations and rotations. In the course of a simple

optimization problem involving, for example, locating a stationary point on the potential energy surface of a small molecule starting from a nearby (very reliable) estimate of its location, such zero Hessian eigenvalues are not a serious problem. The Hessian eigenvectors belonging to the COM displacements and rotations can be identified on the basis of their zero or near-zero eigenvalues and their components removed from the step vector of the surface walking algorithm. In more complex problems, however, the identification and elimination of spurious Hessian eigenmodes may not be so trivial. For example, when using one of the more common surface walking algorithms[1,2] to move from one local minimum (i.e., stable geometry) to another, across one or more saddle points, such an identification may become much more difficult, particularly in a large system having many degrees of freedom. As nonquadratic potential surface features such as points of inflection and side channels (i.e., bifurcations) are encountered, Hessian eigenvalues corresponding to nontrivial modes pass near or through zero. In such cases and in molecules containing many low-frequency internal vibrational modes, the trivial (i.e., COM translation and rotation) and very small nontrivial eigenvalues are very nearly equal; as a result, their eigenvectors become mixed and thus it is difficult to remove the COM motion and rotation from the step vector of the walking algorithm. In these circumstances, it would be quite useful to be able to constrain the surface walking algorithm to automatically avoid moving in an undesired direction.

Thomas and Emerson[4] showed that the so-called Eckart conditions[5] which constrain COM translation and rotation could be conveniently imposed on a Newton–Raphson (NR) surface

(1) C. J. Cerjan and W. H. Miller, *J. Chem. Phys.,* **75,** 2800 (1981); J. Simons, P. Jørgensen, H. Taylor, and J. Ozment, *J. Phys. Chem.,* **87,** 2745 (1983).

(2) J. W. McIver and A. Komornicki, *J. Chem. Soc.,* **94,** 2625 (1972); K. Ishida, M. Morokuma, and A. Komornicki, *J. Chem. Phys.,* **66,** 2153 (1977); T. A. Halgren and W. N. Lipscomb, *Chem. Phys. Lett.,* **49,** 225 (1977).

(3) P. Pulay in "Modern Theoretical Chemistry", H. F. Schaefer III, Ed., Plenum Press, New York, 1977, Chapter 4; P. Jørgensen and J. Simons, *J. Chem. Phys.,* **79,** 334 (1983).

(4) M. W. Thomas and D. Emerson, *J. Mol. Struct.,* **16,** 473 (1973).
(5) C. Eckart, *Phys. Rev.,* **47,** 552 (1935).

walking algorithm[1] by the method of Lagrange multipliers. These and any other constraints of the *linear* form[6]

$$\mathbf{A}^T\omega = 0 \qquad (1)$$

where ω is the step vector of the NR iteration process and $\mathbf{A}$ is a so-called constraint vector (independent of ω) simply add one equation and one variable (the corresponding Lagrange multiplier) to the linear equations of the NR procedure. For such linear constraint equations, the Lagrange multiplier can be evaluated analytically as demonstrated below in section II.

Constraint conditions which are not linear in the step vector ω, however, require numerical evaluation of the corresponding Lagrange multiplier. Such a constraint arises, for example, in implementing the Fletcher surface walking algorithm,[1,7] in which the usual NR formula is modified by the imposition of a step-length constraint quadratic in ω (see section II for details). In this case, there is only one nonlinear condition, and hence the corresponding Lagrange multiplier is easily determined by line-search methods.[1] The simultaneous determination of several such multipliers, however, would constitute a nontrivial multidimensional optimization problem in itself and thus is, in our opinion, to be avoided.

It is of interest, then, to further consider the application of various classes of linear constraints to the NR and closely related algorithms, since most of the commonly employed surface walking procedures are of these forms. Rigorously linear constraints include those eliminating steps along vectors corresponding to COM translations and infinitesimal rotations, as well as the imposition of planes of symmetry. The constraint of quantities which result in conditions nonlinear in the step vector ω, such as bond lengths and angles, may, if the step sizes used in the surface walking procedures can be controlled and kept small, be linearized and thus made computationally tractable. That is, just as the nonlinear finite-rotation constraint may be approximated for small steps by the linear infinitesimal-rotation constraint, other nonlinear conditions may be expanded in ω and truncated at first order. The resulting *linearized* constraints are particularly well suited to the Fletcher constrained-step-length algorithm,[1,7] which can guarantee small relative changes in interatomic distances. In the discussion of section III, exact expressions of the form of eq 1 are obtained for the constraints relating to COM translations and infinitesimal rotations (the Eckart conditions) and for the conservation of a plane of symmetry. Linearized expressions of the same form are then developed for fixing bond lengths, bond angles, substituent group internal rotations, and dihedral angles.

II. Computational Implementation of Linear and Linearized Constraints within Newton and Related Walking Procedures

In the straightforward NR algorithm, the Fletcher[1,7] algorithm, and the various quasi-Newton methods, the potential energy function being optimized is approximated locally by the first three terms of its Taylor series:

$$E(\omega) \approx \tilde{E}(\omega) = E_0 + \mathbf{F}^T\omega + \tfrac{1}{2}\omega^T H\omega \qquad (2)$$

The energy E_0, the gradient F, and the Hessian matrix H can presently all be obtained by quantum chemical methods[3] even for

correlated wave functions. The step vector ω is determined by requiring that $\tilde{E}(\omega)$ be stationary with respect to variation in ω. A set of M constraints of the form of eq 1 may be imposed on ω by subtracting the term $\sum_{i=1}^{M}\lambda_i(\mathbf{A}_i^T\omega)$ from the right-hand side of eq 2 thereby generating a new function to be made stationary with respect to variations in ω. In the case of the Fletcher walking algorithm, the step length $\omega^T\omega$ is also constrained to equal the specified value h^2 through the addition of another Lagrange multiplier term $\lambda/2(h^2 - \omega^T\omega)$ to the right-hand side of eq 2. With the inclusion of both step-*length* and step-direction constraint terms (i.e., terms such as in eq 1), the condition that $\tilde{E}(\omega)$ be stationary with respect to ω reads

$$\nabla_\omega\tilde{E} = 0 = \mathbf{F} - \sum_i^M \lambda_i\mathbf{A}_i - (\lambda I - H)\omega \qquad (3)$$

so the optimal step is given as

$$\omega = (\lambda I - H)^{-1}[\mathbf{F} - \sum_i^M \lambda_i\mathbf{A}_i] \qquad (4)$$

In the absence of any constraints, eq 3 reduces to the familiar NR formula. If the step-length constraint (i.e., λ) is ignored, eq 3 and 4 reduce to the case treated by ref 4.

To find the optimal step vector ω, then, it remains to determine the Lagrange multipliers λ and λ_i, using

$$\partial\tilde{E}/\partial\lambda_i = \mathbf{A}_i^T\omega = 0, \quad i = 1, 2, ..., M \qquad (5)$$

$$\partial\tilde{E}/\partial\lambda = \tfrac{1}{2}(h^2 - \omega^T\omega) \geq 0 \qquad (6)$$

Substitution of eq 4 in to eq 5 yields

$$0 = \mathbf{A}_i^T\omega = \mathbf{A}_i^T(\lambda I - H)^{-1}[\mathbf{F} - \sum_j^M \lambda_j\mathbf{A}_j], \quad i = 1, 2, ..., M \qquad (7)$$

Rearranging eq 7, and defining the $M \times M$ matrix

$$D_{ij} = \mathbf{A}_i^T(\lambda I - H)^{-1}\mathbf{A}_j \qquad (8)$$

and the M vector

$$f_i = \mathbf{A}_i^T(\lambda I - H)^{-1}\mathbf{F} \qquad (9)$$

yields a set of linear equations

$$\sum_j^M D_{ij}\lambda_j = f_i, \quad i = 1,2, ..., M \qquad (10)$$

which (given λ) can be solved to determine the λ_i.

The numerical evaluation of the step-length parameter λ via eq 6, which has been discussed in more detail elsewhere,[1] must be modified slightly to allow for the introduction of the above linear constraints within the Fletcher constrained-step-length algorithm. It should be kept in mind[1] that the solution of eq 6 even in the absence of the linear step-direction constraints (λ_i) involves a nonlinear equation having many branches (i.e., eq 6 with ω from eq 4 is nonlinear in λ). Hence it is instructive to cover briefly how eq 6 is solved when the λ_i are absent.

In the conventional Fletcher algorithm, the step vector ω is first calculated for $\lambda = 0$. If the length of the resulting NR step is *within* the so-called trust radius h, and if the Hessian matrix H has the number of negative eigenvalues appropriate to the stationary point (e.g., minimum or saddle point) toward which one is walking, then this simple NR step is taken. If one or both of these conditions is not met, a line search in λ is carried out until both a step vector ω having length h and a shifted Hessian ($H - \lambda I$) having the proper number of positive and negative eigenvalues are obtained. The introduction of the additional linear constraints described above requires that the calculation of ω at each iteration of the line search (i.e., value of λ) be modified both to generate, via eq 10, new values of the λ_i for each value of λ and to evaluate the square of the step length according to

$$\omega^T\omega = [\mathbf{F}^T - \sum_i^M \lambda_i\mathbf{A}_i^T](\lambda I - H)^{-2}[\mathbf{F} - \sum_i^M \lambda_i\mathbf{A}_i] \qquad (11)$$

Equation 11 differs from the unconstrained step-length expression

---

(6) These linear constraints could be more generally written as $\mathbf{A}^T\omega = c$, where c is a scalar determined at the outset of each iteration. For a linearized constraint, for example, on the cosine of a bond angle (see section IIIc) one might replace eq 30 with

$$(\nabla_\omega \cos\phi)^T\omega + \cos\phi(\omega=0) = \cos\phi_0$$

where $\phi(\omega=0)$ denotes the value of the bond angle at the start of the current potential surface walking iteration, and ϕ_0 is the value of the angle specified at the outset of the surface walk (i.e., the value at which ϕ is to remain fixed). Rather than simply eliminate first-order changes in $\cos\phi$, the above condition would hopefully correct $\cos\phi$ toward the desired value $\cos\phi_0$ as the surface walk proceeded. The use of this form, however, raises questions of stability and of rate of convergence, which we have not yet explored either formally or numerically. For example, see B. van de Graaf and J. M. A. Baas, *J. Comp. Chem.*, **5**, 314–321 (1984).

(7) R. Fletcher, "Practical Methods of Optimization", Vol. 1, Wiley, New York, 1980.

of ref 3 only in that the gradient elements **F** are replaced by a "reduced force"

$$\mathbf{F}_{red} = \mathbf{F} - \sum_{i}^{M} \lambda_i \mathbf{A}_i \qquad (12)$$

Since the inverse matrix $(\lambda I - H)^{-2}$ appearing in eq 11 is the same as that appearing in the unconstrained version, the poles in $\omega^T\omega$ occur where λ coincides with the eigenvalues of H as is the case in the conventional Fletcher process of ref 1 and 7.

Having thus outlined how the line-search methods of ref 1 and 7 can be combined with eq 10 to determine both λ and the $\{\lambda_i\}$ parameters and hence to carry out Fletcher-type potential surface walks, let us turn our attention to formulating each of the constraints mentioned earlier in a form which is linear in ω and which appears as in eq 1.

III. Development of Working Constraint Equations

A. Eckart Conditions. The threefold condition that a step vector of a potential energy surface walking algorithm not translate the COM can be written as

$$\sum_{i=1}^{N} m_i \mathbf{s}_i = \mathbf{0} \qquad (13)$$

where the m_i are the atomic masses, the three vectors $\mathbf{s}_i$ are the corresponding atomic displacements generated by the surface walking procedure, and the index i runs over the N atoms of the system. These equations can be rewritten in the notation used earlier as

$$\mathbf{a}_j^T\omega = 0, \quad j = 1, 2, 3 \qquad (14)$$

where ω is the step vector obtained simply by arranging the $\mathbf{s}_i$ so that

$$\omega_{3(i-1)+j} = (\mathbf{s}_i)_j \qquad (15)$$

where i and j again index the N atoms and the three spatial coordinates, respectively. The three COM translation constraint vectors $\mathbf{a}_j$ have components

$$(\mathbf{a}_j)_k = \sum_{i=1}^{N} \delta_{k,3(i-1)+j} m_i \qquad (16)$$

For example, for $j = 1$ (i.e., the x direction) the $\mathbf{a}_j^T$ vector has elements $(m_1\ 00\ m_2\ 00\ m_3\ 00\ m_4\ 00\ ...\ m_N\ 00)$.

The three infinitesimal rotation constraints can be written as

$$\sum_{i=1}^{N} m_i(\mathbf{r}_i \times \mathbf{s}_i) = \mathbf{0} \qquad (17)$$

where $\mathbf{r}_i$ is the absolute spatial coordinate vector (i.e., in a laboratory-fixed coordinate system) of the ith atom. To express eq 17 in the form shown in eq 1, the three components of the cross product are first written as matrix products:

$$\sum_{i=1}^{N} m_i \mathbf{r}_i^T C^k \mathbf{s}_i = 0, \quad k = 1, 2, 3 \qquad (18)$$

where the elements of the matrices C^k are defined in terms of the Levi–Civita permutation symbol as

$$C_{mn}^k = \epsilon_{kmn} = \begin{cases} 0 \text{ if any two of } k, m, \text{ and } n \text{ are equal} \\ +1 \text{ for } k, m, n \text{ an even permutation of } 1, 2, 3 \\ -1 \text{ for } k, m, n \text{ an odd permutation of } 1, 2, 3 \end{cases} \qquad (19)$$

Next, just as the $\mathbf{s}_i$ were combined to define ω, the elements of the coordinate vectors $\mathbf{r}_i$ are concatenated to define a $3N$ vector **q**

$$\mathbf{q}_{3(i-1)+j} = (\mathbf{r}_i)_j \qquad (20)$$

so that **q** has elements $(r_{1x} r_{1y} r_{1z} r_{2x} r_{2y} r_{2z} ...)$. Finally, eq 18 are rewritten in the desired form

$$\mathbf{q}^T R^k \omega = 0, \quad k = 1, 2, 3 \qquad (21)$$

where the three $3N \times 3N$ matrices R^k are block diagonal, with

the ith 3×3 diagonal subblock of each R^k equal to $m_i C^k$. The structure of **q**, ω, and the R^k is such that when, for example, the product $\mathbf{q}^T R^1 \omega$ is evaluated, the subblock $m_i C^1$ in R^1 is multiplied by those elements of **q** and ω which contain $\mathbf{r}_i$ and $\mathbf{s}_i$, respectively, thereby contributing the term $m_i(\mathbf{r}_i \times \mathbf{s}_i)_x$.

B. Plane of Symmetry Constraints. The requirement that a plane of symmetry be preserved by a step ω imposes $(3N - L)/2$ linear conditions on the step vector ω, where L is the number of atoms which lie within the symmetry plane. Given one unit three-vector $\hat{n}$ normal to the plane (i.e., oriented along the internuclear axis connecting two symmetrically located atoms) and two linearly independent unit three-vectors $\hat{a}$ and $\hat{b}$ orthogonal to $\hat{n}$, the conditions needed to specify reflection symmetry can be written in the form of eq 1 as follows. Any atom (labeled k) lying in the symmetry plane is constrained to remain within the plane by insisting that its displacement have no component along $\hat{n}$:

$$(0,...,0,n_x,n_y,n_z,0,...,0){\cdot}\omega = 0 \qquad (22)$$

Here n_x, n_y, and n_z appear in the positions labeled $3k - 2$, $3k - 1$, and $3k$, respectively. Similarly, each symmetrically located pair of atoms, i and j, not lying in the plane is constrained to move antisymmetrically along $\hat{n}$ and symmetrically along $\hat{a}$ and $\hat{b}$:

$$(0,...,0,n_x,n_y,n_z,0,...,0,n_x,n_y,n_z,0,...,0){\cdot}\omega = 0 \qquad (23)$$

$$(0,...,0,a_x,a_y,a_z,0,...,0,-a_x,-a_y,-a_z,0,...,0){\cdot}\omega = 0 \qquad (24)$$

$$(0,...,0,b_x,b_y,b_z,0,...,0,-b_x,-b_y,-b_z,0,...0){\cdot}\omega = 0 \qquad (25)$$

In the above constraint vectors, the $n_x\ n_y\ n_z$, $a_x\ a_y\ a_z$ and $b_x\ b_y$ b_z elements occur in the positions of the ith and jth atoms.

C. Bond Angle Constraints. All of the above constraint conditions (eq 14, 21–25) involve rigorously linear expressions. The nonlinear condition that a step in a surface walk leave a bond angle unchanged is most conveniently written in terms of the cosine of the angle. To fix the cosine of the angle ϕ between the two internuclear axes joining atom i with atoms j and k, respectively, requires that

$$(\mathbf{r}_j + \mathbf{s}_j - \mathbf{r}_i - \mathbf{s}_i)^T(\mathbf{r}_k + \mathbf{s}_k - \mathbf{r}_i - \mathbf{s}_i)|\mathbf{r}_j + \mathbf{s}_j - \mathbf{r}_i - \mathbf{s}_i|^{-1}|\mathbf{r}_k + \mathbf{s}_k - \mathbf{r}_i - \mathbf{s}_i|^{-1} - (\mathbf{r}_j - \mathbf{r}_i)^T(\mathbf{r}_k - \mathbf{r}_i)|\mathbf{r}_j - \mathbf{r}_i|^{-1}|\mathbf{r}_k - \mathbf{r}_i|^{-1} = 0 \qquad (26)$$

where, as above, $\mathbf{r}_i$ is the absolute position of atom i and $\mathbf{s}_i$ is the corresponding component of the (NR or Fletcher) step vector. Equation 26 can be rewritten in terms of the $3N$-vectors **q** and ω as

$$(\mathbf{q} + \omega)^T Q^{ijki}(\mathbf{q} + \omega)[(\mathbf{q} + \omega)^T Q^{ijji}(\mathbf{q} + \omega) \times (\mathbf{q} + \omega)^T Q^{kiki}(\mathbf{q} + \omega)]^{-1/2} - \mathbf{q}^T Q^{ijki}\mathbf{q}[\mathbf{q}^T Q^{ijji}\mathbf{q}\mathbf{q}^T Q^{kiki}\mathbf{q}]^{-1/2} = 0 \qquad (27)$$

where the $3N \times 3N$ **Q** matrices are defined so that

$$\mathbf{q}^T Q^{ijkl}\mathbf{q} = (\mathbf{r}_i - \mathbf{r}_j)^T(\mathbf{r}_k - \mathbf{r}_l) = \mathbf{r}_i^T\mathbf{r}_k - \mathbf{r}_i^T\mathbf{r}_l - \mathbf{r}_j^T\mathbf{r}_k + \mathbf{r}_j^T\mathbf{r}_l \qquad (28)$$

The matrix Q^{ijkl} defined in eq 28 contains two positive and two negative 3×3 identity matrix subblocks, one of which is associated with each of the four vector dot products in the far right-hand side of eq 28:

$$Q^{ijkl} = \begin{matrix} & & k & & l & \\ & & 0 & & 0 & \\ & & \vdots & & \vdots & \\ i & (0,...,I,...,-I,...,0 \\ & & \vdots & & \vdots & \\ j & 0,...,-I,...,I,...,0 \\ & & \vdots & & \vdots & \\ & & 0 & & 0 & \end{matrix} \qquad (29)$$

If the first term in eq 27 is expanded in a Taylor series around $\omega = \mathbf{0}$, the zeroth-order term in the series cancels the second term in the equation. Keeping only the terms which are first-order in ω generates the *linearized* constraint expression which reads

$$(\nabla_\omega \cos \phi)^T\omega = 0 \qquad (30)$$

where the constraint vector appearing in eq 30 is

$$\nabla_\omega \cos \phi = \{|\mathbf{r}_j - \mathbf{r}_l|^{-1}|\mathbf{r}_k - \mathbf{r}_l|^{-1}(Q^{ijkl} + Q^{kiji}) - \cos \phi(\omega=0) \times$$
$$|\mathbf{r}_j - \mathbf{r}_l|^{-2}Q^{ijji} - \cos \phi(\omega=0)|\mathbf{r}_k - \mathbf{r}_l|^{-2}Q^{kiki}\}\mathbf{q} \quad (31)$$

Imposing eq 30 on the NR or Fletcher formula by means of the method of Lagrange multipliers prevents the resulting step vector from having any component along the 3N-vector $\nabla_\omega \cos \phi$ which lies tangent, at $\mathbf{q}$, to the curve generated by finite variation of the bond angle ϕ.

D. Bond-Length Constraints. The requirement that the distance between atoms i and j remains unchanged by a step is easily written as

$$|\mathbf{r}_j + \mathbf{s}_j - \mathbf{r}_i - \mathbf{s}_i|^2 - |\mathbf{r}_j - \mathbf{r}_i|^2 = 0$$

or

$$2(\mathbf{r}_j - \mathbf{r}_i)^T(\mathbf{s}_j - \mathbf{s}_i) + |\mathbf{s}_j - \mathbf{s}_i|^2 = 0 \quad (32)$$

In terms of $\mathbf{q}$ and ω, this expression can be written as

$$2\mathbf{q}^TQ^{ijji}\omega + \omega^TQ^{ijji}\omega = 0 \quad (33)$$

which is straightforwardly linearized by neglecting the second term

$$\mathbf{q}^TQ^{ijji}\omega = 0 \quad (34)$$

The Q^{ijji} matrix was defined earlier in eq 28–29.

E. Constrained Rotation of a Substituent Group. Given a molecule in which the terminal atoms i, j, and k (e.g., the three H atoms in CH_3) are each bonded to an atom l which is in turn attached to the rest of the molecule by a bond to atom m, the angle of rotation of the ijk group (e.g., CH_3 group rotation) around the l–m bond axis is a curvilinear coordinate. The linearized condition to constrain first-order variation in this rotation angle can be expressed in terms of the components of the torques $(\mathbf{r}_h \times \mathbf{s}_h)$ for each atom $(h = i, j, k)$ along the l,m bond axis

$$\sum_{h=ijk} [(\mathbf{r}_h - \mathbf{r}_l) \times (\mathbf{r}_l - \mathbf{r}_m)]^T\mathbf{s}_h = 0 \quad (35)$$

Rewriting eq 35 in the form of eq 1 yields the desired linearized constraint condition

$$(0,...,a_x,a_y,a_z,0,...,b_x,b_y,b_z,0,...,c_x,c_y,c_z,0,...)\cdot\omega = 0 \quad (36)$$

where the three vectors appearing in eq 36 are defined by

$$\mathbf{a} = (\mathbf{r}_i - \mathbf{r}_l) \times (\mathbf{r}_l - \mathbf{r}_m) \quad (37a)$$

$$\mathbf{b} = (\mathbf{r}_j - \mathbf{r}_l) \times (\mathbf{r}_l - \mathbf{r}_m) \quad (37b)$$

$$\mathbf{c} = (\mathbf{r}_k - \mathbf{r}_l) \times (\mathbf{r}_l - \mathbf{r}_m) \quad (37c)$$

The components a_x, b_x, and c_x are located in the $(3i - 2)$th, $(3j - 2)$th, and $(3k - 2)$th elements, respectively, of the constraint vector of eq 36.

F. Dihedral Angle Constraints. We now consider a molecule in which atoms i, j, k, and l are bonded together in sequence. The dihedral angle τ between the plane containing atoms i, j, and k and the plane containing atoms j, k, and l is, like the bond length and bond angle coordinates considered above, nonlinear in the space-fixed atomic Cartesian coordinates. As was done for bond angles, an expression of the form of eq 30 can be developed for the first-order constraint of variations in the cosine of the dihedral angle. The cosine of the angle τ can be written as

$$\cos \tau = (\mathbf{v}_{kj} \times \mathbf{v}_{ij})^T(\mathbf{v}_{lk} \times \mathbf{v}_{kj})|\mathbf{v}_{kj} \times \mathbf{v}_{ij}|^{-1}|\mathbf{v}_{lk} \times \mathbf{v}_{kj}|^{-1} \quad (38)$$

where the three vectors $\mathbf{v}_{mn}$ are defined in terms of the absolute positions $\mathbf{r}$ and the displacements $\mathbf{s}$ of the respective atoms:

$$\mathbf{v}_{mn} = \mathbf{r}_m + \mathbf{s}_m - \mathbf{r}_n - \mathbf{s}_n \quad (39)$$

By means of the identity

$$(\mathbf{a} \times \mathbf{b})^T(\mathbf{c} \times \mathbf{d}) = (\mathbf{a}^T\mathbf{c})(\mathbf{b}^T\mathbf{d}) - (\mathbf{a}^T\mathbf{d})(\mathbf{b}^T\mathbf{c}) \quad (40)$$

eq 39 is rewritten as

$$\cos \tau = [(\mathbf{v}_{kj}^T\mathbf{v}_{lk})(\mathbf{v}_{ij}^T\mathbf{v}_{kj}) - |\mathbf{v}_{kj}|^2(\mathbf{v}_{ij}^T\mathbf{v}_{lk})][[\mathbf{v}_{kj}|^2|\mathbf{v}_{ij}|^2 -$$
$$(\mathbf{v}_{kj}^T\mathbf{v}_{ij})^2]^{-1/2}[|\mathbf{v}_{lk}|^2|\mathbf{v}_{kj}|^2 - (\mathbf{v}_{lk}^T\mathbf{v}_{kj})^2]^{-1/2} \quad (41)$$

which can then be rewritten in terms of the 3N vectors $\mathbf{q}$ and ω:

$$\cos \tau = [(\mathbf{q} + \omega)^TQ^{kjlk}(\mathbf{q} + \omega)(\mathbf{q} + \omega)^TQ^{ijkj}(\mathbf{q} + \omega) -$$
$$(\mathbf{q} + \omega)^TQ^{kjkj}(\mathbf{q} + \omega)(\mathbf{q} + \omega)^TQ^{ijlk}(\mathbf{q} + \omega)][(\mathbf{q} +$$
$$\omega)^TQ^{kjkj}(\mathbf{q} + \omega)(\mathbf{q} + \omega)^TQ^{ijij}(\mathbf{q} + \omega) -$$
$$((\mathbf{q} + \omega)^TQ^{kjij}(\mathbf{q} + \omega))^2]^{-1/2}[(\mathbf{q} + \omega)^TQ^{klk}(\mathbf{q} + \omega) \times$$
$$(\mathbf{q} + \omega)^TQ^{kjkj}(\mathbf{q} + \omega) - ((\mathbf{q} + \omega)^TQ^{lkkj}(\mathbf{q} + \omega))^2]^{-1/2} \quad (42)$$

where the notation of section IIIC has again been employed. Finally, as was done to express the first-order angle constraint as $(\nabla_\omega \cos \phi)^T\omega = 0$, we need to evaluate the gradient of τ with respect to ω at the point $\omega = 0$.

$$\nabla_\omega \cos \tau = \nabla_\omega(AB^{-1/2}C^{-1/2}) = B^{-1/2}C^{-1/2}(\nabla_\omega A) -$$
$$\tfrac{1}{2}AB^{-3/2}C^{-1/2}(\nabla_\omega B) - \tfrac{1}{2}AB^{-1/2}C^{-3/2}(\nabla_\omega C) \quad (43)$$

where A, B, and C are the three scalar quantities which are each enclosed in square brackets in eq 41, and again in eq 42, and

$$\nabla_\omega A(\omega=0) = (\mathbf{q}^TQ^{kjlk}\mathbf{q})(Q^{ijkj} + Q^{kjij})\mathbf{q} + (\mathbf{q}^TQ^{ijkj}\mathbf{q})(Q^{kjlk} +$$
$$Q^{lkkj})\mathbf{q} - (\mathbf{q}^TQ^{kjkj}\mathbf{q})(Q^{ijlk} + Q^{lkij})\mathbf{q} - 2(\mathbf{q}^TQ^{ijlk}\mathbf{q})(Q^{kjkj}\mathbf{q}) \quad (44)$$

$$\nabla_\omega B(\omega=0) = 2(\mathbf{q}^TQ^{kjkj}\mathbf{q})Q^{ijij}\mathbf{q} + 2(\mathbf{q}^TQ^{ijij}\mathbf{q})Q^{kjkj}\mathbf{q} -$$
$$2(\mathbf{q}^TQ^{kjij}\mathbf{q})(Q^{kjij} + Q^{ijkj})\mathbf{q} \quad (45)$$

$$\nabla_\omega C(\omega=0) = 2(\mathbf{q}^TQ^{klk}\mathbf{q})Q^{kjkj}\mathbf{q} + 2(\mathbf{q}^TQ^{kjkj}\mathbf{q})Q^{klk}\mathbf{q} -$$
$$2(\mathbf{q}^TQ^{lkkj}\mathbf{q})(Q^{lkkj} + Q^{kjlk})\mathbf{q} \quad (46)$$

Equations 44–46 can also be written as

$$\nabla_\omega A(\omega=0) = \{\mathbf{v}_{kj}^T\mathbf{v}_{lk}(Q^{ijkj} + Q^{kjij}) + \mathbf{v}_{ij}^T\mathbf{v}_{kj}(Q^{kjlk} + Q^{lkkj}) -$$
$$|\mathbf{v}_{kj}|^2(Q^{ijlk} + Q^{lkij}) - 2\mathbf{v}_{ij}^T\mathbf{v}_{lk}Q^{kjkj}\}\mathbf{q} \quad (47)$$

$$\nabla_\omega B(\omega=0) = \{2|\mathbf{v}_{kj}|^2Q^{ijij} + 2|\mathbf{v}_{ij}|^2Q^{kjkj} - 2\mathbf{v}_{kj}^T\mathbf{v}_{ij}(Q^{kjij} + Q^{ijkj})\}\mathbf{q} \quad (48)$$

$$\nabla_\omega C(\omega=0) =$$
$$\{2|\mathbf{v}_{lk}|^2Q^{kjkj} + 2|\mathbf{v}_{kj}|^2Q^{klk} - 2\mathbf{v}_{lk}^T\mathbf{v}_{kj}(Q^{lkkj} + Q^{kjlk})\}\mathbf{q} \quad (49)$$

where, since the gradient is evaluated at $\omega = 0$

$$\mathbf{v}_{mn} = \mathbf{r}_m - \mathbf{r}_n \quad (50)$$

involves simply the interatomic position vectors.

IV. Summary and Discussion

In this paper we have shown how to, within any of the conventionally employed potential energy surface walking algorithms, impose geometrical constraints involving center-of-mass motion, rigid-body and internal rotations, bond lengths and angles (including dihedral angles), and symmetry planes. All of these constraints can be written, in linearized forms which are valid for small step lengths, as $\mathbf{A}^T\omega = 0$ where A is a constraint vector which depends upon the specific kind of constraint being imposed and ω is the Cartesian step vector of length 3N. The constraint vectors $\{\mathbf{A}_i\}$ pertaining to each of the cases mentioned above are explicitly given in eq 16, 21, 22–25, 31, 34, 36, and 43.

To implement any or all of the constraints treated here, one first must obtain values for the local gradient **F** and Hessian *H* elements in terms of the 3N Cartesian coordinates describing the locations of the N atoms. We assume that such information is available either from ab initio or semiempirical quantum chemical calculations or from empirical force-field methods. Next one must compute the constraint vectors $\{\mathbf{A}_i\}$ relevant to every constraint to be imposed. These vectors depend, as can be seen clearly by inspecting the equations mentioned above, on the local geometry of the molecule and the masses of its constituent atoms. Next, the *D* matrix of eq 8 can be formed for whatever value of λ is appropriate (in the NR algorithm, $\lambda = 0$, in the Fletcher algorithm, the optimal choice for λ must be determined iteratively as discussed in earlier work from our lab (see ref 1) and eq 10 can then be solved for the Lagrange multipliers $\{\lambda_i\}$ associated with each constraint. Finally, the step vector ω can be evaluated by using eq 4 and the molecule's atomic centers can be displaced by amounts contained in ω to generate the next point in the potential surface walk. This step-by-step walking process can be continued until, at a local minimum or saddle point, the gradient vector

vanishes and hence convergence is reached.

As mentioned in the Introduction, it may not be necessary to utilize the kind of automated constraint algorithm developed here when treating walks on potential surfaces characterizing small molecules; in such cases, one can simply allow the Newton–Raphson, Fletcher, etc. algorithm to generate step vectors ω which contain COM and rotational displacements and then trivially remove these undesired components. However, when dealing with multidimensional surfaces which possess nontrivial nearly zero Hessian eigenvalues (e.g., for low-frequency vibrational modes or small curvatures arising near inflection points or bifurcation points), it is, in our opinion, important to remove the undesired

motions automatically and before the walking algorithm has a chance to become "confused" by their presence. The method put forth here permits one to achieve this goal and to thereby generate surface walks which maintain the desired geometrical constraints throughout.

Effects of Temperature on Oscillatory Behavior in the Bromate–Bromide–Manganous System[1]

Enio Kumpinsky and Irving R. Epstein*

Department of Chemistry, Brandeis University, Waltham, Massachusetts 02254 (Received: March 30, 1984)

Experiments have been carried out to assess the influence of temperature on the behavior of a minimal bromate oscillator ($BrO_3^- - Br^- - Mn^{2+}$ in a continuously stirred tank reactor). The results are compared with calculations performed by using the NFT mechanism supplemented by a plausible set of activation energies. The oscillatory range is found to be extremely sensitive to the values of certain rate constants, some of which do not significantly influence the domain of bistability. The agreement between the experimental and calculated amplitude and period as functions of temperature is quite good.

Introduction

The study of oscillating chemical reactions has until quite recently been dominated by the Belousov–Zhabotinskii reaction in particular and, more generally, by the class of bromate-driven oscillators. The discovery of inorganic bromate oscillators[2-7] has served both to broaden the scope of oscillatory behavior and to facilitate the development of mechanistic understanding. In fact, the "minimal bromate oscillator",[5] consisting of bromate, bromide, and a one-electron redox couple (Ce^{3+}/Ce^{4+} or Mn^{2+}/Mn^{3+}) in a stirred tank reactor (CSTR), has been referred to[6] as "the simplest chemical oscillator fully understood in terms of elementary reactions".

With the exception of a single set of experiments,[6] all studies of the minimal bromate oscillator have been carried out at a single fixed temperature. A stringent test of the mechanistic understanding which has been claimed for this system would be to investigate its behavior as a function of temperature and to see whether that behavior can be modeled by the assumed mechanism with a reasonable set of activation energies.

We present here such a study, in which the reaction of BrO_3^-, Br^-, and Mn^{2+} in a CSTR has been studied both experimentally and computationally over a range of temperatures and flow rates. We discuss the extent of oscillatory behavior, the variation of amplitude and period with temperature, and the choice of a set of activation energies that enables us to achieve good agreement

TABLE I: Range of k_j over Which Oscillations Are Obtained[a] at 25 °C

	k_j		
j	$a^{b,e}$	b^c	$c^{d,e}$
1	2.00	2.1 M^{-3} s^{-1}	2.26
−1	0	10^4 M^{-1} s^{-1}	1.9×10^7
2	1.86×10^9	2×10^9 M^{-2} s^{-1}	2.10×10^9
−2	0	5×10^{-5} M^{-1} s^{-1}	4.2×10^3
3	2.0×10^9	8×10^9 M^{-2} s^{-1}	2.4×10^{11}
−3	0	110 s^{-1}	4.5×10^2
4	9.6×10^3	1×10^4 M^{-1} s^{-1}	1.04×10^4
−4	1.78×10^7	2×10^7 M^{-1} s^{-1}	2.94×10^7
5	1.50×10^5	1.806×10^5 M^{-2} s^{-1}	1.91×10^5
−5	2.13×10^7	2.4×10^7 M^{-1} s^{-1}	3.94×10^7
6	0	34.56 M^{-1} s^{-1}	1.0×10^4
−6	0	1.3×10^{-4} M^{-3} s^{-1}	2.75×10^{-3}
7	0	4×10^7 M^{-1} s^{-1}	6.4×10^{10}
−7	0	2.1×10^{-10} M^{-2} s^{-1}	1.3×10^{-2}

[a] $[BrO_3^-]_0 = 6.5 \times 10^{-3}$ M, $[Br^-]_0 = 1.0 \times 10^{-4}$ M, $[Mn^{2+}]_0 = 1.02 \times 10^{-4}$ M, $[H^+]_0 = 1.5$ M. [b] Lowest value for which oscillations are obtained. Units as in column b. [c] Value at 25 °C from ref 10. [d] Highest value for which oscillations are obtained. Units as in column b. [e] Note that eq 8 and 9 hold only for column b and not for columns a and c.

with the observed behavior using the model developed earlier to describe the system at 25 °C.

Experimental Section

The experiments were carried out in a Pyrex CSTR of a design described previously.[7] Because the Teflon cap employed in the earlier experiments had a coefficient of thermal expansion significantly different from that of the glass reactor, a new, all-glass reactor-cap system was built that had a volume of 19.5 cm³. Temperature regulation to better than 0.1 °C was achieved by using a Forma Model 2095-2 bath and circulator in conjunction

(1) Part 23 in the series "Systematic Design of Chemical Oscillators". Part 22: Maselko, J.; Epstein, I. R. *J. Phys. Chem.* **1984**, *88*, 5305.
(2) Adamčikova, L.; Ševčik, P. *Int. J. Chem. Kinet.* **1982**, *14*, 735.
(3) Orbán, M.; Epstein, I. R. *J. Phys. Chem.* **1983**, *87*, 3212.
(4) Alamgir, M.; Orbán, M.; Epstein, I. R. *J. Phys. Chem.* **1983**, *87*, 3725.
(5) Orbán, M.; De Kepper, P.; Epstein, I. R. *J. Am. Chem. Soc.* **1982**, *104*, 2657.
(6) Bar-Eli, K.; Geiseler, W. *J. Phys. Chem.* **1983**, *87*, 3769.
(7) De Kepper, P.; Epstein, I. R.; Kustin, K. *J. Am. Chem. Soc.* **1981**, *103*, 6121.