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Identification of Reaction Products and Stoichiometry of the Overall Process in the Methylmalonic Acid Belousov–Zhabotinsky Oscillator. A ^{1}H NMR Study

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By using ^{1}H NMR the main products in the methylmalonic acid Belousov–Zhabotinsky reaction were found to be bromomethylmalonic acid (BrMeMA) and acetic acid, besides formic acid, and traces of undefined products. When the reaction is complete, the final concentration ratio between BrMeMA and acetic acid was found to be [BrMeMA]/[CH$_3$COOH] = 1.5, which is predicted by the Field–Körös–Noyes (FKN) theory. The stoichiometry between reactant and recorded product concentrations is in excellent agreement with the FKN theory.

Introduction

In recent years chemical oscillating systems have been an area of increasing interest. Among the chemical oscillating reactions, the classical[1] Belousov[2]–Zhabotinsky[3] (BZ) reaction is probably one of the most studied and best understood systems. Notably by the work of Field, Körös, and Noyes[4] (FKN) the essential mechanism is now well established. Although the FKN mechanism was originally proposed for the case when malonic acid is used as an organic substrate, the mechanism is generally believed to be valid also for other classical BZ oscillators using different catalysts or organic substrates.[5]

However, there is still a considerable lack in the understanding of the organic reactions taking place in these systems. For the malonic acid oscillator, FKN proposed carbon dioxide, formic acid, and bromomalonic acid (BrMA) as the main end products of the reaction with a final stoichiometric ratio between BrMA and formic acid of 3:2 (reaction 1).

$$3BrO_3^- + 5CH_2(COOH)_2 + 3H^+ \rightarrow$$
$$3CHBr(COOH)_2 + 2HCOOH + 4CO_2 + 5H_2O \quad (1)$$
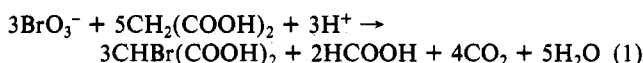
However, several reports showed, using quite different techniques, that formic acid is not an end product in the malonic acid system.[6–8] This deviation from process 1 may be due to the presence of very reactive oxybromine species.

Recently, a classical BZ oscillator using methylmalonic acid (MeMA) as an organic substrate was reported.[9] A mechanistic study of this oscillator appears to be of some interest, since the MeMA system is not so reactive as the malonic acid oscillator.[9] In addition only one brominated product is expected, which probably should also lead to a "cleaner" mechanism.

The present paper presents an identification of reaction products in the Ce(IV)-catalyzed MeMA BZ system using ^{1}H NMR spectroscopy. The main end products were found to be bromomethylmalonic acid (BrMeMA) and acetic acid. The final concentration ratio observed between BrMeMA and acetic acid was found to be [BrMeMA]/[CH$_3$COOH] = 1.5, exactly as originally

predicted for the analogous malonic acid BZ reaction by the Field–Körös–Noyes theory.

Materials and Method

Proton high-resolution NMR spectroscopy is a frequently applied method when studying organic components in solution. The different components are usually identified by routine qualitative spectral analysis.[10] In the present work the end products of the MeMA BZ oscillator have been identified by adding a convenient amount of the component in question to the reaction mixture.

As a quantitative tool, NMR has the advantage that a pure sample of the sought substance is not necessary. The most useful aspect is the accurate proportionality between the integrated signal intensity and the number of resonating hydrogen nuclei, a fact that makes it possible to follow the concentrations of different organic compounds in situ and continuously vs. time.

Two main conditions that may influence the success of quantitative measurements are (i) the spin–lattice relaxation time, T_1, and (ii) the dynamical range of the instrument.[10]

The longest T_1 measured in the MeMA oscillating system (by using the usual inversion recovery technique) was found to be 3.6 s (the acetic acid component). Without going into technical details, it is the spin relaxation time which mainly defines the instrumental parameters during a single record.

The dynamic range limits the ratio between the highest and lowest observed intensity peaks. It is purely an instrumental effect. Thus, to hold the solvated proton peak (here, the highest intensity peak) as low as possible, 1 M D$_2$SO$_4$ in D$_2$O as solvent has been used.

The ^{1}H spectra were obtained on a pulse FT NMR spectrometer, Bruker CXP 200, operating in the quadrature mode at a ^{1}H frequency of 200 MHz. Sixteen scans for each record were accumulated over a bandwidth of 1.5 kHz with 16K data points and a 35° pulse angle.

The reagents were of analytical grade, except the MeMA, which was of *purum* quality (>99%, Fluka). All chemicals were used without further purification. All experiments were performed at 25 °C. The reacton volume was 0.75 mL (the spectrometer was equipped with a 5-mm probe). The reactants were always mixed in the following order: 1 M D$_2$SO$_4$/D$_2$O, MeMA, (NH$_4$)$_2$Ce(NO$_3$)$_6$, and finally KBrO$_3$. The following initial concentrations were used: 0.28 M MeMA, 0.1 M KBrO$_3$, and 2.1 × 10^{-3} M Ce(IV). All spectra were obtained with sample spinning and continuous stirring throughout the experiment.

Experimental data points (concentration vs. time) were fitted to a three-parameter exponential curve, $Y_i = A \times \exp(BX_i) + C$,

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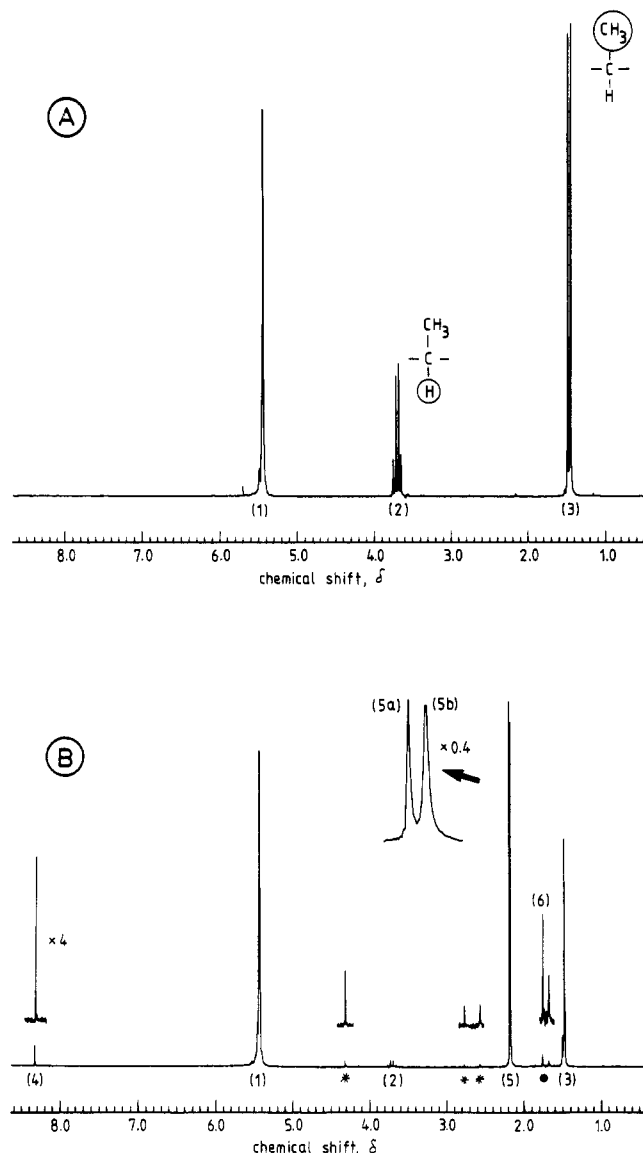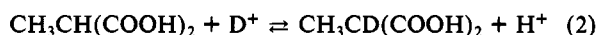(9) Ruoff, P.; Schwitters, B. *Z. Phys. Chem. (Wiesbaden)* **1983**, *135*, 171.

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Figure 1. (A) ^{1}H NMR spectrum of the reactants. (1) Signal from the protons of the two carboxyl groups in MeMA. (2) Quartet corresponding to the coupling of the proton attached to the central C atom in MeMA with the methyl group. (3) Doublet corresponding to the coupling of the methyl group with the central proton. (B) ^{1}H NMR spectrum of the products. Due to the incorperation of deuterium into MeMA, the quartet (2) disappears and (3) becomes a singlet. (4) Formic acid top. (5) Composite signal consisting of the acetic acid peak (5a) and the BrMe-MA peak (5b). (6) Most intense signal of the unknown species (*).

using a nonlinear iteration procedure[11] with *B* as the iteration parameter.

The only species identified but not followed by NMR were carbon dioxide and carbon monoxide. Carbon dioxide was detected by leading the produced gas through a saturated Ba(OH)$_2$ solution, while carbon monoxide was detected by using the palladium chloride test.[12]

Results and Discussion

When MeMA is dissolved in D$_2$SO$_4$, we observe that the hydrogen atom attached to the central carbon atom in MeMA is gradually replaced by deuterium, schematically written as

$$CH_3CH(COOH)_2 + D^+ \rightleftarrows CH_3CD(COOH)_2 + H^+ \quad (2)$$

However, this additional effect is not of importance in our present study.

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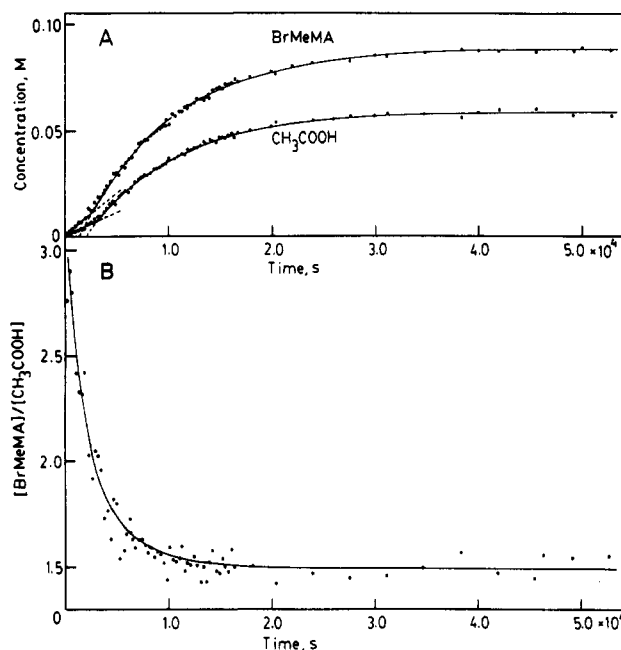(12) Bayer, F.; Wagner, G. "Die chemische Analyse"; Enke: Stuttgart, 1960; Band 39.

Figure 2. (A) Increase of BrMeMA and acetic acid concentrations with time. The breakpoint in the beginning indicates the end of the induction period. (B) Concentration ratio between BrMeMA and acetic acid as a function of time.

TABLE I: Record of Concentrations

time, s	[methylmalonic acid],[a] M	[BrMeMA], M	[CH$_3$COOH], M
0.0	0.280	0.0	0.0
282.0	0.267	0.000855	0.000311
582.0	0.270	0.00241	0.000830
882.0	0.267	0.00363	0.00130
1182.0	0.261	0.00472	0.00195
1482.0	0.269	0.00647	0.00278
1782.0	0.253	0.00675	0.00291
2082.0	0.249	0.00865	0.00358
2382.0	0.241	0.0134	0.00660
2682.0	0.243	0.0129	0.00672
2982.0	0.250	0.0162	0.00791
38382.0	0.118	0.0886	0.0590
41982.0	0.117	0.0878	0.0598
45582.0	0.116	0.0875	0.0584
49182.0	0.116	0.0887	0.0572
52782.0	0.110	0.0887	0.0572

[a] Sum of deuterated and undeuterated acids.

The ^{1}H NMR spectra of the reactants and the products in the MeMA BZ reaction are given in Figure 1 together with the identifications of the peaks. The accumulation of acetic acid and BrMeMA during a run is shown in Figure 2A, while Figure 2B gives the corresponding ratio between BrMeMA and acetic acid concentrations. When the reaction is complete, the concentration ratio between BrMeMA and acetic acid is found to be 1.5.

It is interesting that FKN's thermodynamic analysis of the malonic acid system proposed the same ratio, with BrMA and formic acid as the analogous species.[4] However, while the much more reactive malonic acid system shows some deviation from the proposed process given by eq 1 (i.e., formic acid is neither formed nor consumed in the malonic acid system),[6–8] it seems that for the MeMA BZ reaction an analogous overall reaction as described by eq 1 can be formulated, i.e.

$$3BrO_3^- + 5CH_3CH(COOH)_2 + 3H^+ \rightarrow$$
$$3CH_3CBr(COOH)_2 + 2CH_3COOH + 4CO_2 + 5H_2O \quad (3)$$
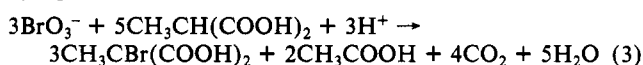
We will now show that not only the relative concentration ratio between BrMeMA and acetic acid is in agreement with the stoichiometry of process 3 but also experimentally determined absolute concentrations of MeMA, BrMeMA, and acetic acid are properly described by this reaction. In Table I, some of the

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

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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

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