Characterization of a manganese-catalyzed bromate-driven oscillator within the proton NMR framework

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of 8×10^2 M^{-2} s^{-1}. Our observed value of 8×10^4 M^{-1} s^{-1} for

$$BrO_3^- + HOI + H^+ \rightarrow HBrO_2 + HIO_2 \qquad (R7)$$

process R6 suggests that HOI reacts 100 times as rapidly with the HMP as with bromate (both bromate and HMP are present in equal concentrations). In fact, if one considers processes R6 and R7 as two parallel pseudo-first-order reactions with equal bromate and HMP concentrations in a 1 M sulfuric acid medium, it can be easily shown that 99% ($=100k_6/(k_6 + k_7)$) of the initially available HOI reacts according to process R6, while only 1% ($=100k_7/(k_6 + k_7)$) reacts with bromate ion, thus preventing effective oxidation of HOI by bromate.

The fate and importance of the product(s) of process R6, which has not been identified yet, is still a subject of speculations. They may affect the autocatalytic production of HBrO$_2$ in the oscillator as previously suggested,[11] or might subsequently release iodine compounds in oxidation states 0 or –I which could react with HOBr and form bromide ion, which is the control intermediate of the oscillations.[12] The decrease in the iodine absorbance (Figure 4) indicates that the product(s) of process R6 should contain bonded iodine, because otherwise the absorbance would not decrease. It appears that HOI reacts as an iodination rather than as an oxidizing agent.

It might even be possible that reaction R6 could induce the generation of organic radicals[12,19] in a similar way as metal ion catalysts do.[2-5] In this case the iodine-catalyzed bromate oscillators would be analogous to the metal ion catalyzed bromate oscillators.

(19) Roedig, A. In *Methoden der Organischen Chemie (Houben-Weyl)*; Vierte Auflage, Band V/4, Halogenverbindungen; Müller, E., Ed.; Thieme: Stuttgart, 1960; p 558.

Characterization of a Manganese-Catalyzed Bromate-Driven Oscillator within the 1H NMR Framework

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The oscillating behavior of Mn^{2+} in a manganese-catalyzed bromate-driven oscillator with methylmalonic acid as the organic substrate is shown to induce corresponding oscillations in the following NMR parameters: chemical shift, line width, and the spin–lattice relaxation rate of the solvent water protons. The induction period and period lengths derived from such NMR experiments are found to be in qualitative agreement with results obtained by potentiometric measurements. One major advantage with the NMR technique is the potential of monitoring the NMR absorption of the organic species to follow the degradation of methylmalonic acid to bromomethylmalonic acid and acetic acid in situ as the oscillations proceed. The sum of the concentrations of these three species is found to be constant, as suggested by earlier measurements. A value for the enolization rate constant of methylmalonic acid is determined ($(4.87 \pm 0.29) \times 10^{-5}$ s^{-1}) and found to be in agreement with previous values.

Introduction

The addition of small amounts of paramagnetic salts to pure water has a marked effect on the nuclear spin relaxation rates of water protons as measured by 1H NMR[1] and was first considered theoretically by Bloembergen, Purcell, and Pound.[2] Later, Dickinson[3] observed that the chemical shift of the water signal is also affected by paramagnetic impurities as previously suggested theoretically by Purcell.[4]

These effects make nuclear magnetic resonance a powerful analytical tool in studying redox reactions, complex formation, precipitation reactions, and even reaction kinetics—in which paramagnetic ions participate—if the overall reaction is accompanied by a change in the effective magnetic moment or a change in the concentration of paramagnetic species.[5,6]

A 1H NMR study of a malonic acid (MA) Belousov–Zhabotinsky (BZ) reaction was reported by Schlüter and Weiss in 1981.[7] In its general form, a Belousov–Zhabotinsky system[8,9] is a met-

al-ion-catalyzed oxidation of easily brominated organic material by bromate ions in aqueous acidic media.[10] To pursue the time oscillation of the spin–lattice relaxation rate of the solvent water protons, the commonly used Ce^{3+}/Ce^{4+} catalyst was replaced by a Mn^{2+}/Mn^{3+} catalyst due to its much stronger paramagnetic influence on the relaxation time of the water protons. In fact, the interaction of the paramagnetic ion Ce^{3+} with the water protons is much too weak to be observable by the NMR technique.

In this report we extend the work presented in ref 7 substantially by demonstrating that oscillations in a manganese-catalyzed

(1) Bernheim, R. A.; Brown, T. H.; Gutowsky, H. S.; Woessner, P. E. *J. Chem. Phys.* **1959**, *30*, 950.
(2) Bloembergen, N.; Purcell, E. M.; Pound, R. V. *Phys. Rev.* **1948**, *73*, 679.
(3) Dickinson, W. C. *Phys. Rev.* **1951**, *81*, 717.
(4) Bloembergen, N.; Dickinson, W. C. *Phys. Rev.* **1950**, *79*, 179.
(5) Notnagel, K. H.; Weiss, A. *Ber. Bunsen-Ges. Phys. Chem.* **1970**, *74*, 659.
(6) Schlüter, A.; Weiss, A. *Z. Phys. Chem. (Munich)* **1977**, *105*, 267.
(7) Schlüter, A.; Weiss, A. *Ber. Bunsen-Ges. Phys. Chem.* **1981**, *85*, 306.
(8) Belousov, B. P. *Ref. Radiats. Med., Moscow* **1958**, 145.
(9) Zhabotinsky, A. M. *Dokl. Akad. Nauk SSSR* **1964**, *157*, 392.
(10) Noyes, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 4644.

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MeMA BZ oscillator can be investigated by measuring the corresponding oscillations in the spin–lattice relaxation rate as well as oscillations in line width and chemical shift of the solvent water protons. Moreover, the induction period and period lengths inferred from these NMR data will be shown to be in qualitative agreement with the corresponding parameters obtained by potentiometric measurements. One advantage of the NMR technique, demonstrated in this and previous work,[11] is the potential of following the accumulation and consumption of the main organic species in situ during the oscillations.

Theory

Two independent time signals (intensity vs time) denoted the transversal magnetization, $M_{xy}(t)$, and the longitudinal magnetization, $M_z(t)$, are traditionally measured by NMR by the so-called spin-echo and inversion-recovery experiments.[12] Considering only the signal arising from the solvent water protons in paramagnetic liquid solutions, the two magnetizations can be written

$$M_{xy}(\tau) = M_0 \exp(-\tau/T_2) \qquad (1)$$

$$M_z(\tau) = M_0(1 - 2\exp(-\tau/T_1)) \qquad (2)$$

where M_0 is the equilibrium magnetization, $1/T_2$ and $1/T_1$ define the spin–spin and spin–lattice relaxation rates, respectively, and τ is time. For paramagnetic solutions these NMR parameters are mainly controlled by the interaction between the electronic spin of the paramagnetic ion and the nuclear spin of the neighboring water proton.[13-16] However, if the concentration of the paramagnetic ion is relatively low, the interaction between the nuclear spins of the water protons (the diamagnetic contribution) must be considered as well. A simple relation exists between the overall relaxation rate and the paramagnetic concentration C.

$$X = a_x C + X_{\text{diamagnetic}}; \quad X = 1/T_1, 1/T_2 \qquad (3)$$

By Fourier transforming the transversal magnetization, eq 1, the corresponding frequency signal or spectrum $L(\nu)$ is obtained[12]

$$L(\nu) = L(0)\frac{(\Delta\nu_{1/2})^2}{(\Delta\nu_{1/2})^2 + 4\nu^2} \qquad (4)$$

where ν is frequency and $\Delta\nu_{1/2}$ is the full width at half-height of the Lorentzian function $L(\nu)$. It is now easy to see that $\Delta\nu_{1/2}$ is related to the spin–spin relaxation rate $1/T_2$ by the equation

$$\Delta\nu_{1/2} = 1/\pi T_2 \qquad (5)$$

which is valid only for purely Lorentzian (and purely Gaussian) functions.[17] In general, the frequency at which the Lorentzian function attains its maximum is measured relative to a suitable reference compound where the corresponding frequency difference is termed the chemical shift (δ). In this work chemical shift will be reported in hertz. Dickinson[3] and later Swift and Connick[18] showed that the chemical shift of the solvent water protons in paramagnetic solutions could be described by an expression analogous to eq 3.

$$\delta = a_\delta C + \delta_{\text{diamagnetic}} \qquad (6)$$

where $\delta_{\text{diamagnetic}}$ defines the chemical shift of the solvent water

protons for $C = 0$. For water protons in aqueous solutions containing a paramagnetic ion the interaction between the electronic spin of the paramagnetic ion and the proton spin of the neighboring proton nuclei is about 1000 times more effective than the corresponding spin–spin interaction between neighboring water protons (dipole–dipole coupling), which implies that if the concentration (C) of paramagnetic ions is not too low the diamagnetic contribution to the NMR parameters will be negligible.

In the MeMA BZ oscillator studied in this work only two paramagnetic ions are involved, namely, Mn^{2+} and Mn^{3+}. Thus, the paramagnetic relaxation rates and the paramagnetic chemical shift can be written

$$X = k_x(Mn^{3+})C_{Mn^{3+}} + k_x(Mn^{2+})C_{Mn^{2+}} \qquad (7)$$

where $X = x = \delta$, $1/T_1$, $1/T_2$ and the "magnetic coefficients" $k_x(Mn^{2+})$ and $k_x(Mn^{3+})$ are constants. By introducing the mass balance equation

$$C_0 = C_{Mn^{2+}} + C_{Mn^{3+}} \qquad (8)$$

where C_0 is the initial Mn^{2+} concentration, eq 7 becomes

$$X = k_x(Mn^{3+})C_0 + (k_x(Mn^{2+}) - k_x(Mn^{3+}))C \qquad (9)$$

where $X = x = \delta$, $1/T_1$, $1/T_2$ and $C = C_{Mn^{2+}}$. Oscillations in the respective NMR parameters would therefore be expected to take place if

$$k_x(Mn^{2+}) \neq k_x(Mn^{3+}); \quad X = x = \delta, 1/T_1, 1/T_2$$

One should also keep in mind that the +3 oxidation state of the manganese ion is not generally stable in aqueous solutions.[19] However, by use of a solvent containing phosphoric acid, Mn^{3+} is partially stabilized by complexation with phosphate.

Experimental Section

The BZ reaction was run in a polarographic cell at room temperature (25 °C) with a reaction volume of 50 mL. Oscillations were followed potentiometrically with an uncalibrated platinum electrode. A standard double-junction calomel electrode was used as a reference. The potentials were measured and recorded by a two-channel x/t recorder. If not otherwise stated, the reaction mixture was exposed to a N_2 atmosphere and was stirred by means of a magnetic stirrer at approximately 1400 rpm.

The ^1H NMR spectra were obtained on a FT-NMR spectrometer, Bruker CXP-200, operating at 200 MHz (proton). One scan for each record was accumulated by using a bandwidth of 2 kHz with 1K data points. Two different types of experiments were performed alternatively on the same sample; a T_1 measurement and a line width/chemical shift measurement. The program was set up to do an initial T_1 experiment, followed by recording a simple single-pulse spectrum (FID). After a fixed time delay of approximately 5 s, another T_1 measurement was performed and the same cycle was repeated for about 2.5 h.

By measuring $M(\tau)$ at various times τ, one can calculate $1/T_1$ from eq 2. However, in the MeMA BZ oscillating system the magnetization is also a function of the reaction time t. By rearranging eq 2

$$\frac{1}{T_1(t)} = -\frac{1}{\tau}\ln\left(\frac{1}{2}\left(1 - \frac{M(\tau,t)}{M_0}\right)\right) \qquad (10)$$

$1/T_1$ can be determined at any time t during the reaction by measuring $M(\tau,t)$ and keeping τ fixed. This procedure of determining T_1 is generally termed nuclear magnetic resonance titration (NMRT)[7] and will be used throughout in this work. The equilibrium magnetization M_0 was determined independently on a reference solution containing all the actual species except the $KBrO_3$ salt.

All NMR spectra determined in this work have been analyzed by a curve-fitting procedure in order to determine line form, line width (at half-height), and chemical shift. Due to the paramagnetic line broadening, we found it essential to calculate the

(11) Hansen, E. W.; Gran, H. C.; Ruoff, P. *J. Phys. Chem.* **1985**, *89*, 682.

(12) Abraham, R. J.; Lofthus, P. *Proton and Carbon-13 NMR Spectroscopy. An Integrated Approach*; Heyden and Son: London, 1978.

(13) Zimmerman, J. A. *J. Chem. Phys.* **1954**, *22*, 950.

(14) Bloembergen, N. *J. Chem. Phys.* **1957**, *27*, 572.

(15) Bloembergen, N. *J. Chem. Phys.* **1957**, *27*, 595.

(16) Morgan, L. O.; Nolle, A. W. *J. Chem. Phys.* **1959**, *31*, 365.

(17) Rushworth, F. A.; Tunstall, D. P. *Nuclear Magnetic Resonance*; Gordon and Breach: New York, 1973.

(18) Swift, T. J.; Connick, R. E. *J. Chem. Phys.* **1962**, *37*, 307.

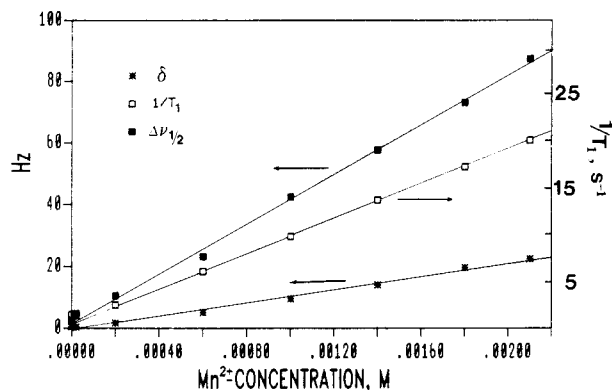(19) Meyer, J.; Marek, J. *Z. Anorg. Chem.* **1924**, *133*, 325.

Figure 1. Observed spin–lattice relaxation rate $(1/T_1)$, chemical shift (δ), and line width $(\Delta\nu_{1/2})$ of the solvent water peak vs Mn^{2+} concentration in 0.28 M MeMA dissolved in 1 M H_3PO_4. Solid lines are calculated by a linear least-squares fit to the observed data.

position of the water peak by such a curve-fitting procedure in order to obtain reliable chemical shift and line-width data.[20] An additional objective of the line-shape analysis is to verify if the water peak is purely Lorentzian (eq 4) in order to estimate the spin–spin relaxation time T_2 from eq 5.

The reagents used were of analytical grade, except the MeMA which was of purum quality (>99%, Fluka; Switzerland). The chemicals were used without further purification and were always mixed in the order 0.28 M MeMA, 0.2 M $KBrO_3$, and 2.1 × 10^{-3} M $MnSO_4$ dissolved in 1 M H_3PO_4. As mentioned before, the addition of phosphoric acid is to stabilize the Mn^{3+} ion formed during the reaction.[19]

The reaction volume was 0.75 mL (the spectrometer was equipped with a 5-mm-diameter probe) and contained about 10% D_2O for the purpose of locking the sample. The deuterium lock is the means by which long-term stability of the magnetic field is achieved. All experiments have been performed at room temperature (20 °C), and the spectra were obtained with sample spinning and continuous stirring throughout the experiment in order to avoid or minimize spatial oscillations. The solution was kept under an inert atmosphere of N_2.

Results and Discussion

Equations 3 and 6 have been verified for Mn^{2+} solutions containing 0.28 M MeMA in 1 M H_3PO_4 by varying the Mn^{2+} concentration from 0 to 21 × 10^{-4} M in order to establish the sensitivity and inherent uncertainty in the NMR variables and to confirm the validity of the expected Lorentzian line shape of the water peak, eq 4, which is essential in order to calculate the spin–spin relaxation rate from eq 5. One other reason for performing an initial experiment of this kind is the distinct dependence of the NMR parameters on the magnetic field strength.[13,16] All spin–lattice relaxation time measurements were determined by applying the NMRT technique (eq 10) with τ = 30 ms. The results are summarized in Figure 1 and suggest a maximum change in the three NMR variables $\Delta\nu_{1/2}$, $1/T_1$, and δ of approximately 87 Hz, 20 s^{-1}, and 22 Hz, respectively. The chemical shift of the water peak was measured relative to the water peak position in a solution of 0.28 M MeMA acid dissolved in 1 M H_3PO_4. The corresponding relative uncertainties were estimated to be 3.1%, 2.8%, and 11%, respectively. The line-shape analysis revealed purely Lorentzian absorption curves rendering the spin–spin relaxation rate $1/T_2$ attainable from eq 5.

The value of T_2 determined from eq 5 was inspected by performing a spin-echo (Carr–Purcell,[21] Meiboom–Gill[22]) experiment, eq 1, on a solution containing 2.1 × 10^{-3} M $MnSO_4$ and 0.28 M MeMA dissolved in 1 M H_3PO_4, and the value 3.74 ±0.01 ms was found to be in excellent agreement with the value of 3.65 ±
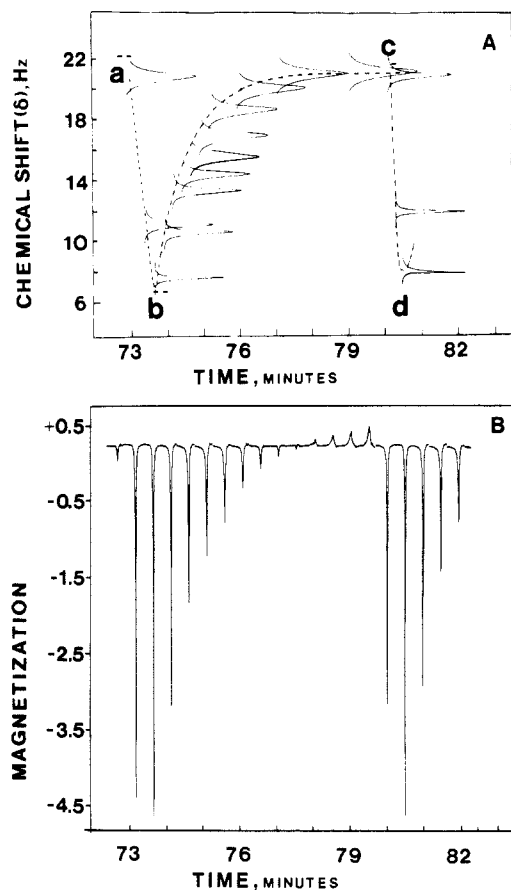
(20) Weiss, G. H.; Ferretti, J. A.; Kiefer, J. E. *J. Magn. Reson.* **1982,** *46,* 69.
(21) Carr, H. Y.; Purcell, E. M. *Phys. Rev.* **1954,** *94,* 630.
(22) Meiboom, S.; Gill, D. *Rev. Sci. Instrum.* **1958,** *29,* 688.


Figure 2. Variation of the (A) chemical shift (δ) and line width and (B) the magnetization $M(\tau$ = 30 ms, $t)$, eq 10, of the solvent water peak vs reaction time (t) of one oscillating period in a MeMA BZ oscillating system; 0.28 M MeMA, 0.2 M $KBrO_3$, and 2.1 × 10^{-3} M $MnSO_4$ dissolved in 1 M H_3PO_4/H_2O. The different segments of the dotted line in (A) were calculated by a nonlinear least-squares fit $\Delta\nu_{1/2}$ = A exp$(-Bt)$ + C with B as the iteration parameter. The monotonic increase in chemical shift with time (bc) is connected with the reduction of Mn^{3+} → Mn^{2+}, while the sudden steep decrease in the shift (ab and cd) is connected with the much faster autocatalytic oxidation of Mn^{2+} → Mn^{3+}. The oscillation of the observed magnetization depicted in (B) is measured by the NMRT technique; see text for further details.

0.11 ms obtained from the line-width measurement (eq 5) and reflects the rather good magnetic field homogeneity. Moreover, the observed T_1/T_2 ratio was found to be constant (13.76 ± 0.14) and independent of the Mn^{2+} concentration, which is an additional support of the validity of eq 3 with $X_{diamagnetic}$ = 0. Unfortunately, a similar investigation on pure Mn^{3+} solutions was not possible due to severe difficulties in oxidizing Mn^{2+} quantitatively to stable Mn^{3+}.[19]

Oscillatory Behavior of a MeMA BZ Oscillator within the NMR Framework

Oscillation in line width and chemical shift of the solvent water peak generated by oscillation of the catalyst concentration in a MeMA BZ oscillator is demonstrated in Figure 2A for one oscillating period. The corresponding observed oscillation of the longitudinal magnetization M_z (τ = 30 ms, $t)$ vs reaction time is illustrated in Figure 2B by implementing the NMRT technique. A limited but representative selection (240) of the total number of data points (1000) for the first 43 oscillations are depicted in Figure 3 showing the spin–lattice relaxation rate, derived from eq 10 with M_0 = 10 units, and line width vs chemical shift. The linear one-to-one correspondence between the three NMR parameters illustrates that oscillations in the catalyst concentration can be followed equally well by detecting any one of the three NMR variables. Information concerning induction periods and length of oscillating periods or the time variation in catalyst concentration vs reaction time will be identical and independent
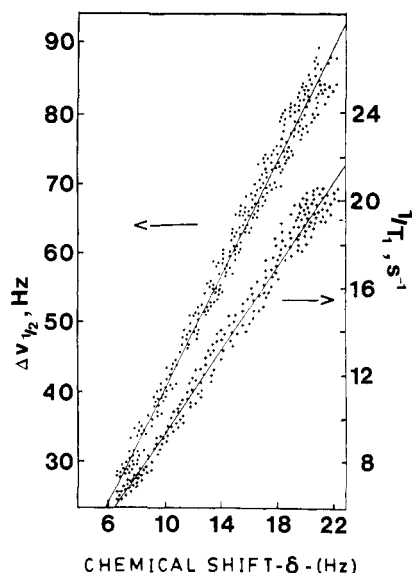
Figure 3. Line width ($\Delta\nu_{1/2}$) and spin–lattice relaxation rate ($1/T_1$) vs chemical shift (δ) of the solvent water peak in a MeMA BZ oscillator. The solid lines were calculated by a linear least-squares fit. Initial concentrations of reagents were 0.28 M MeMA, 0.2 M KBrO$_3$, and 2.1 × 10^{-3} M MnSO$_4$ dissolved in 1 M H$_3$PO$_4$/H$_2$O. A given point in the figure represents two of the NMR parameters measured at the same instant of time during the oscillating reaction.

of the choice of NMR parameter. On the other hand, the line width covers a significantly broader frequency range (26–87 Hz) than, for example, the corresponding chemical shift domain which is only 16 Hz. Equivalently, the spin–spin relaxation rate will change between 89 and 273 s^{-1} while the spin–lattice relaxation rate is encountered in the range 6.3–20.3 s^{-1}. Taking into account the inherent experimental uncertainty in each of the three NMR parameters, we conclude that the line width (or spin–spin relaxation rate) is the more sensitive of the three NMR parameters. Another advantage of using the spin–spin relaxation rate is that the paramagnetic contribution is much larger than the diamagnetic contribution, which is only approximately 2 s^{-1} and implies that the spin–spin relaxation rate or line width of the solvent water protons in the oscillating system is mainly affected by the paramagnetic interaction and only marginally influenced by the diamagnetic contribution. With this in mind we find it appropriate and advantageous to consider mainly the line-width measurements in the subsequent discussion.

The observed increase in the spread of the data points with increasing chemical shift, as shown in Figure 3, is mainly caused by the increasing uncertainty in the chemical shift and line width due to a significant broadening of the water peak with increasing Mn^{2+} concentration. The observed line width vs reaction time for the first three oscillation periods is plotted in Figure 4A and defines an induction period of 7.75 min, which corresponds rather well with the analogous time found from potentiometric measurements of approximately 7.5 min (Figure 4). The reproducibility of the observed NMR line widths is within 15%. The change in Mn^{2+} concentration vs reaction time is also depicted in Figure 4A and will be discussed in more detail later in this work. The period length, which is observed to increase with reaction time (Figure 5), is in qualitative agreement with corresponding data found by potentiometric measurements.[23] The reason for the pronounced dispersion in period length vs oscillation number is probably due to fluctuations in temperature and stirring rate. In all the NMR experiments performed in this study, a thin, asymmetric glass rod was lowered into the solution and kept fixed while the glass tube and liquid sample were spinning with a constant rate of approximately 1800 rpm. The intrinsic or "effective" stirring rate was, however, undetermined. Moreover, significant fluctuations in stirring rate vs reaction time might easily arise in
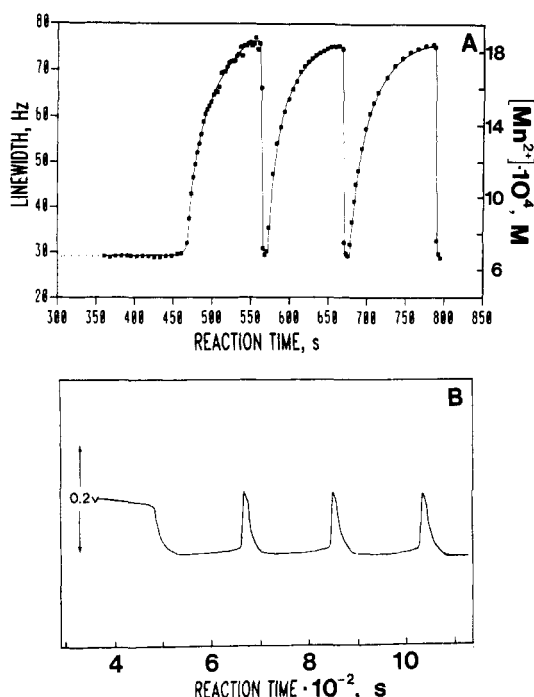
(23) Ruoff P.; Schwitters, B. *Z. Phys. Chem. (Munich)* **1983**, *135*, 171.

Figure 4. (A) Line width ($\Delta\nu_{1/2}$) of the solvent water peak vs reaction time (t) for the first three oscillations in a MeMA BZ reaction. The different segments of the solid line were determined by a nonlinear least-squares fit ($\Delta\nu_{1/2} = A\exp(-Bt) + C$). The Mn^{2+} concentration is calculated from eq 3 with $a_{\Delta\nu_{1/2}} = (2.515 \pm 0.0460) \times 10^{-5}$ Hz M^{-1} and $X_{\text{diamagnetic}} = 0$. (B) Initial oscillations of a MeMA BZ oscillating reaction followed potentiometrically by a platinum electrode indicating the change in Mn^{2+} concentration vs time. Initial concentrations of reagents in both experiments were 0.28 M MeMA, 0.2 M KBrO$_3$, and 2.1 × 10^{-3} M MnSO$_4$ dissolved in 1 M H$_3$PO$_4$/H$_2$O.
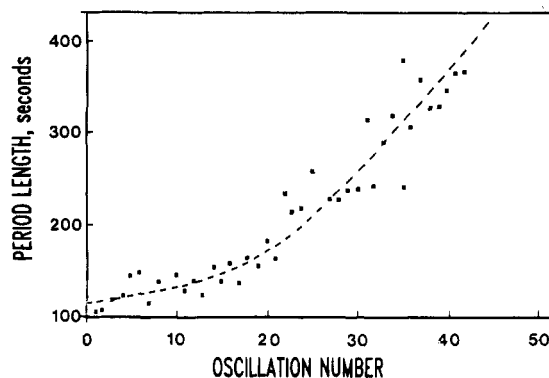

Figure 5. Period length vs oscillation number in a MeMA BZ oscillator determined by NMR (Figure 4A). Initial concentration of reagents were 0.28 M MeMA, 0.2 KBrO$_3$, and 2.1 × 10^{-3} M MnSO$_4$ dissolved in 1 M H$_3$PO$_4$/H$_2$O.

the NMR experiment and result in an increased scatter of the observed period lengths vs time (Figure 5). This statement is supported by the observed sensitivity of period length vs stirring rate as measured potentiometrically (Figure 6). In this experiment the period length of the first oscillation was measured as a function of stirring rate of identical solutions containing 2.1 × 10^{-3} M MnSO$_4$, 0.2 M KBrO$_3$, and 0.28 M MeMA dissolved in 1 M H$_3$PO$_4$.

An analogous spread in the observed NMR line widths is also seen in Figure 7, which exhibit the maximum ($\Delta\nu_{1/2,\text{max}}$) and minimum ($\Delta\nu_{1/2,\text{min}}$) line width in each oscillation vs oscillation number. The reason for the more pronounced scatter in $\Delta\nu_{1/2,\text{max}}$ compared to $\Delta\nu_{1/2,\text{min}}$ cannot be explained by fluctuations in stirring rate (which would influence these parameters equally) but is simply related to the increasing uncertainty in the measurement of line width with increasing Mn^{2+} concentration (broader lines). The results depicted in Figure 7 indicate a steady increase of the maximum Mn^{2+} concentration in each oscillation period vs reaction
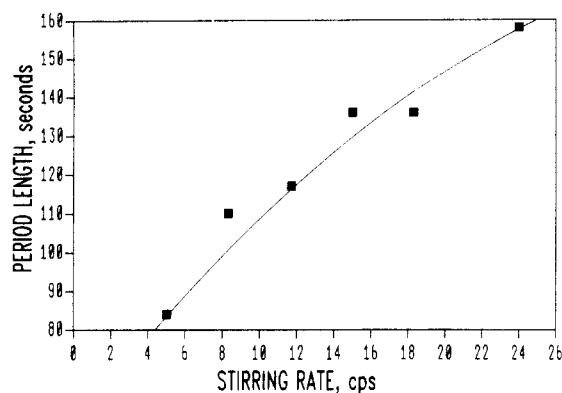
Figure 6. Period length (first oscillation) vs stirring rate of a MeMA BZ reaction determined potentiometrically. Solid line represents an eyeball fit to the experimental data points. Initial concentrations of reagents were 0.28 M MeMA, 0.2 M KBrO₃, and 2.1 × 10⁻³ M MnSO₄ dissolved in 1 M H₃PO₄/H₂O.
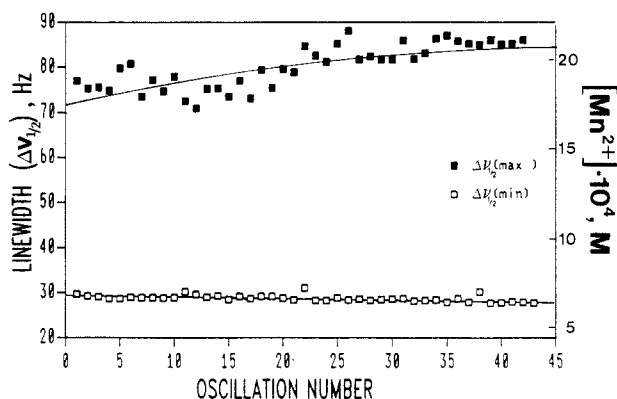

Figure 7. Extreme values $\Delta\nu_{1/2,max}$ and $\Delta\nu_{1/2,min}$ of the solvent water peak in each oscillation period vs oscillation number. Solid lines represent eyeball fits to the observed data points. The Mn²⁺ concentration is calculated from eq 3 with $a_{\Delta\nu_{1/2}}$ = (2.515 ± 0.0460) × 10⁻⁵ Hz M⁻¹ and $X_{diamagnetic}$ = 0. Initial concentration of reagents were 0.28 M MeMA, 0.2 KBrO₃, and 2.1 × 10⁻³ M MnSO₄ dissolved in 1 M H₃PO₄/H₂O.

time and suggest that the maximum concentration of Mn²⁺ in each oscillation increases asymptotically toward the value 2.1 × 10⁻³ M. This value of the Mn²⁺ concentration is estimated by comparing the observed line width of the solvent water peak in the oscillating reaction (Figure 7) with the corresponding line width estimated from the "reference" solution in Figure 1. The approximate increase in the maximum concentration of Mn²⁺ between the first and the last oscillating period is close to 15%.

An analogous investigation of the observed $\Delta\nu_{1/2,min}$ of each oscillation period vs oscillation number (or reaction time) shows a line width that is nearly constant and equal to 29.2 Hz. A more refined analysis reveals, however, a small but significant reduction in $\Delta\nu_{1/2,min}$ as a function of oscillation number, indicating that the maximum Mn³⁺ concentration in each oscillating period vs reaction time is increasing. This observation should inevitably lead to a similar change in the extreme value of the catalyst concentration ratio $r(extreme)$ = ([Mn²⁺]/[Mn³⁺])$_{extreme}$ vs time. However, such a behavior is not observed potentiometrically. The potentiometric data suggest that $r(extreme)$ is constant and independent of reaction time, which might be explained by a very small variation of $r(extreme)$ vs time—a variation which is masked by the logarithmic nature of the potentiometric technique. These experimental results therefore do not necessarily reveal any inconsistency between the two experimental techniques.

Catalyst Concentration

If the "magnetic coefficients" of the two paramagnetic ions Mn²⁺ and Mn³⁺ are known, the concentration of each of them in a chemical oscillator can be determined from eq 7 and 8. Unfortunately, as already mentioned, the magnetic coefficient of the Mn³⁺ ion complex is neither experimentally nor theoretically
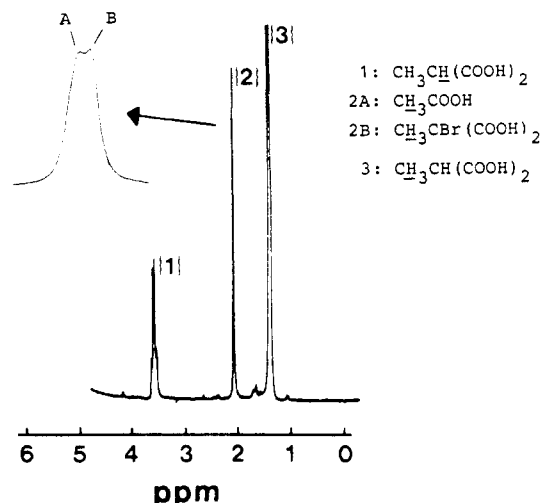

Figure 8. Example of a ¹H NMR spectrum of reactants and products in a manganese-catalyzed MeMA BZ oscillator at some time t during the reaction. The much bigger and broader absorption peak of the solvent water peak at δ = 5.22 ppm in the spectrum is removed for cosmetic reasons only. (1) "Quartet" corresponding to the coupling of the protons attached to the central C atom with the methyl group in methylmalonic acid (CH₃CH(COOH)₂). (2) "Composite" signal consisting of the acetic acid peak (A) and the bromomethylmalonic acid peak (B). (3) "Doublet" peak corresponding to the coupling of the methyl group with the central proton in methylmalonic acid (CH₃CH(COOH)₂). Initial concentrations of reagents were 0.28 M MeMA, 0.2 M KBrO₃, and 2.1 × 10⁻³ M MnSO₄ dissolved in 1 M H₃PO₄/H₂O.

available. However, the observed ratio of T_1 and T_2 for the solvent water protons during the oscillating reaction is found to be constant (13.35 ± 0.28) and approximately equal to the ratio of $k_{1/T_2}(Mn^{2+})$ and $k_{1/T_1}(Mn^{2+})$ of 13.75 ± 0.14. In short

$$T_1/T_2 = k_{1/T_2}(Mn^{2+})/k_{1/T_1}(Mn^{2+}) \qquad (11)$$

By replacing the relaxation times T_1 and T_2 on the left side of eq 11 with the corresponding expressions given by eq 9, it is easy to derive the following relations

$$k_{1/T_2}(Mn^{2+})/k_{1/T_2}(Mn^{3+}) = k_{1/T_1}(Mn^{2+})/k_{1/T_1}(Mn^{3+}) \qquad (R1)$$

$$k_x(Mn^{3+}) \ll k_x(Mn^{2+}); \quad x = 1/T_1, 1/T_2 \qquad (R2)$$

We have not found any additional experimental or theoretical data that can establish which one of the relations (R1) or (R2) is correct. Actually, both of them might simultaneously satisfy the empirical eq 11. (R1) defines no unambiguous correlation between the NMR relaxation rates and C, the concentration of Mn²⁺. However, (R2) does. Relation R2 simply states that the paramagnetic influence of the Mn³⁺ ion complex on the NMR properties of the solvent water protons is negligible compared to the case of the Mn²⁺ ion. Inserting (R2) into eq 9 gives eq 3, which implies that C, the concentration of Mn²⁺, can be estimated vs time in the chemical oscillator as well. From the results presented in Figure 1, $a_{\Delta\nu_{1/2}}$ = (2.515 ± 0.046) × 10⁻⁵ Hz M⁻¹ and $\Delta\nu_{1/2,diamagnetic}$ ≅ 0. Equation 3 has been used to estimate C, and the results are depicted in Figures 4A and 7.

Concentration of the Main Organic Species in the MeMA BZ Oscillator

A typical ¹H NMR spectrum of a manganese-catalyzed methylmalonic acid BZ oscillator at some time t during the reaction is shown in Figure 8 together with an identification of the different main organic species involved. The initial concentrations were as follows: 0.28 M MeMA, 0.2 M KBrO₃, and 2.1 × 10⁻³ M MnSO₄ dissolved in 1 M H₃PO₄. Note the two overlapping peaks at δ = 2.07 ppm which represent the methyl protons in bromomethylmalonic acid (BrMeMA) and acetic acid (HAc), respectively. These peaks were identified by adding acetic acid and bromomethylmalonic acid to the solution at time t = ∞ (equilibrium). The severe overlapping is due to the paramagnetic line
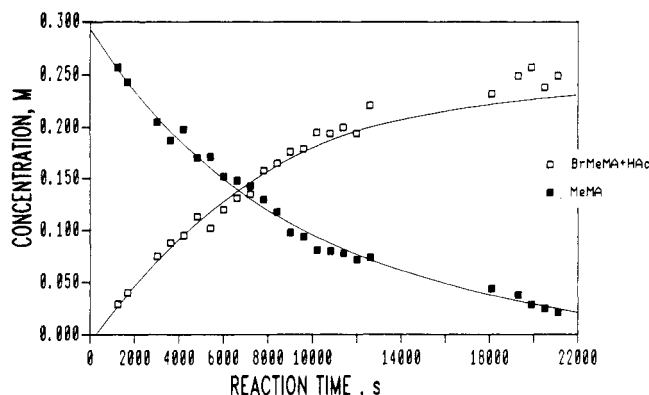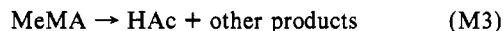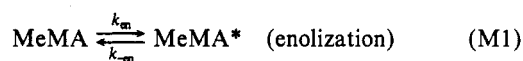
Figure 9. Concentration vs time of the main organic species in a MeMA BZ oscillator determined by ^{1}H NMR. The solid curves were calculated by a nonlinear least-squares fit to eq 12 and 13. Initial concentrations of reagents were 0.28 M MeMA, 0.2 M KBrO$_3$, and 2.1 × 10^{-3} M MnSO$_4$ dissolved in 1 M H$_3$PO$_4$/H$_2$O.

broadening which makes it difficult—and in some cases impossible—to resolve the two peaks quantitatively. The doublet peak at δ = 1.38 ppm arises from the methyl protons on methylmalonic acid (MeMA), which are coupled to the single proton on the central carbon. The poorly resolved quartet at δ = 3.61 ppm represents the single proton in MeMA which is coupled to the three equivalent protons in the methyl group of MeMA. Because of the accurate proportionality between the integrated intensity (area) of a NMR peak and the number of resonating nuclei, the NMR technique makes it possible to follow the different organic compounds in situ and continuously vs reaction time. The intensity of the methyl protons in MeMA at time t = 1230 s was set equal to 100, and the sum of the intensities of all the methyl groups detected in the NMR spectra at all times was found to be constant and equal to 108.5 ± 3.0. This intensity or area (108.5) was associated with the initial concentration of the MeMA acid (0.28 M) so that the concentrations of the other main organic species were determined at any time during the reaction from this estimated proportionality factor (0.002 57). Unfortunately, it was impossible to separate the overlapping peaks resulting from BrMeMA and HAc so only the sum of concentrations of these species was extractable. The results are shown in Figure 9.

By considering the following simplified model of the production of BrMeMA and HAc[24]

$$MeMA \underset{k_{-en}}{\overset{k_{en}}{\rightleftharpoons}} MeMA^* \quad \text{(enolization)} \qquad \text{(M1)}$$

$$MeMA^* + Br_2 \rightarrow BrMeMA + Br^- + H^+ \qquad \text{(M2)}$$

$$MeMA \rightarrow HAc + \text{other products} \qquad \text{(M3)}$$

and assuming that the enol form is in a steady-state concentration, $(d/dt)[MeMA^*] = 0$, the following approximate solutions are found

(24) Hansen, E. W.; Ruoff, P., submitted for publication in *J. Phys. Chem.*

$$[MeMA] = C_0' \exp(-K_{MeMA}t) \qquad (12)$$

$$X = X_\infty(1 - \exp(-\tfrac{5}{3}K_{en}t)); \quad X = [BrMeMA] + [HAc] \qquad (13)$$

where $K_{en} = k_{en}[H^+]$ defines the enolization rate of methylmalonic acid and the ratio of [BrMeMA] and [HAc] is assumed to be constant and equal to 1.5.[11] The principle of deriving the enolization rate from NMR measurements—as just outlined—is carefully explained in ref 24 and will therefore not be discussed any further in this report. Such information is not easily available from potentiometric measurements and reflects one important advantage of the NMR technique.

The solid curves in Figure 9 were calculated by a nonlinear least-squares fit to eq 12 and 13 with K_{MeMA} and K_{en} as the iteration parameters respectively. Taking into account the simplifications and assumptions involved in the estimation of $K_{en} = (4.87 \pm 0.29) \times 10^{-5}$ s^{-1}, this value of the enolization rate is in acceptable agreement with the results published elsewhere ($K_{en} = 5.40 \times 10^{-5}$ s^{-1}).[23-25] By assuming the overall reaction of the main organic species to follow the FKN mechanism[11,26] i.e.

$$3BrO_3^- + 5MeMA + 3H^+ \rightarrow$$
$$3BrMeMA + 2HAc + 4CO_2 + 5H_2O$$
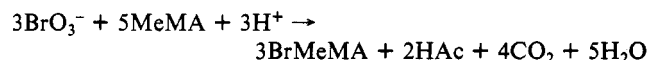
the final or equilibrium concentration of the sum of BrMeMA and HAc would be identical with 0.28 M, which is in good agreement with the value 0.290 ± 0.009 M determined from eq 13. The relative uncertainty in the determination of concentration derived from the NMR peak intensity was estimated to be 3%.

Concluding Remarks

Spectral resolution can be improved by either reducing the initial Mn^{2+} concentration or decreasing the magnetic field strength[13] (increasing the spin–spin relaxation time T_2). Unfortunately, both of these operations will cause a reduction in the sensitivity of the NMR variables (chemical shift, line width, and spin–lattice relaxation rate) due to a narrowing of the range of change of these parameters. In addition, a decrease in the magnetic field strength will lead to a reduction in the S/N ratio. There is therefore no simple way of enhancing the spectral resolution and at the same time conserve the sensitivity in the NMR parameters. However, it is in general possible to improve the S/N ratio by choosing a deuteriated solvent, as for example 1 M H$_3$PO$_4$ in D$_2$O, in order to keep the residual water peak as low as possible and thereby enhancing the dynamic range. A number of such experiments have been carried out with success.[11,24,25] The NMR method discussed in this report should in general be applicable to other oscillating chemical reactions where Mn^{2+} oxidation is taking place, for instance, to investigate the role of Mn^{2+} in trypsin oscillations.[27]

(25) Hansen, E. W.; Ruoff, P. *J. Phys. Chem.* **1988**, *92*, 2641.
(26) Field, R. J.; Körös, E.; Noyes, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 8649.
(27) Vajda, T. *Cryo-Lett.* **1986**, *7*, 23.