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No Formic Acid Production or Consumption in the Malonic Acid Belousov–Zhabotinsky Reaction. Quantitative Experimental Evidence by Hydrogen-1 Nuclear Magnetic Resonance

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The use of ^{1}H-NMR spectroscopy was found to be a powerful tool in analyzing both quantitatively and qualitatively the different organic components in Belousov–Zhabotinsky systems. Using this technique, we found further evidence of the inertness of formic acid in the Ce(IV)-catalyzed malonic acid Belousov–Zhabotinsky reaction.

Notably by the work of Noyes[1] and co-workers, the Belousov[2]–Zhabotinsky[3] (BZ) reaction is one of the most investigated and best understood chemical oscillating systems. However, there is still a considerable lack in the understanding of the organic reaction subset taking place in the BZ reaction.

Most of the present experimental methods used in analyzing the organic components are rather qualitative in nature, making a quantitative estimate difficult. The use of ^{1}H-NMR spectroscopy with mixtures of D_2SO_4, D_2O, and H_2O as solvent was found to be a powerful tool in analyzing *both qualitatively and quantitatively* the different organic reaction products in the BZ systems.[4] Studying the methylmalonic acid BZ reaction[5] by this method, we were able to follow the main products, acetic acid and bromomethylmalonic acid (BrMeMA), in the course of the reaction besides small amounts of formic acid. The final concentration ratio between BrMeMA and acetic acid was found to be $[BrMeMA]/[CH_3COOH] = 1.5$ with the overall reaction of the methylmalonic acid oscillator proceeding with the same stoichiometry as originally proposed by the Field–Körös–Noyes (FKN) mechanism![4,6] For the malonic acid system, however, additional complexities arise. For this system, the work of Hess and co-workers indicated that formic acid is not an end product.[7] With our rather good agreement of the methylmalonic acid oscillator with the FKN theory in mind, we found it therefore natural to investigate, by means of the ^{1}H-NMR technique, (a) how much formic acid is actually formed as an end product (if any at all) and (b), alternatively, if formic acid is consumed when added initially to the malonic acid BZ system.

In agreement with previous reports,[7,8] we found that formic acid is not an end product in the Ce(IV)-catalyzed malonic acid BZ reaction. The detection limit was better than 10^{-4} M in formic acid. Initial concentrations of reactants are given in Table I.

Using different initial amounts of formic acid, while keeping the other reactant concentrations constant, we found no significant change in the formic acid concentration, showing that formic acid is an *inert* component in the malonic acid BZ reaction. A typical run is shown in Table I.

TABLE I: Data Illustrating the Inertness of Formic Acid in the BZ System[a]

time, s	$C_{\text{formic acid}}$, M	time, s	$C_{\text{formic acid}}$, M
570	0.010 50	5670	0.011 62
870	0.011 56	5970	0.011 03
1170	0.011 18	6270	0.010 95
1470	0.011 02	6570	0.011 18
1770	0.011 76	6870	0.011 02
2070	0.011 28	7170	0.011 82
2370	0.011 46	7470	0.011 45
2670	0.011 53	7770	0.010 87
2970	0.011 28	8070	0.011 24
3270	0.011 16	8370	0.011 27
3570	0.011 43	8670	0.011 18
3870	0.011 08	12270	0.011 44
4170	0.011 12	15870	0.010 78
4470	0.011 63	19470	0.011 52
4770	0.011 13	23070	0.011 75
5070	0.011 29	26670	0.011 31
5370	0.011 22	30270	0.011 40

[a] Initial concentrations: $C^\circ_{\text{malonic acid}} = 0.28$ M; $C^\circ_{(NH_4)_2Ce(NO_3)_6} = 2.1 \times 10^{-3}$ M; $C^\circ_{KBrO_3} = 0.1$ M; $C^\circ_{D_2SO_4}$ (D_2O as solvent) = 1.0 M; $C^\circ_{\text{formic acid}} = 0.0112$ M; $T = 298$ K. The deviation of formic acid concentration from its initial value (0.0112 M) is less than 4.5% at any time. (The estimated uncertainty in each measurement of concentration is less than 5%.)

The inertness of formic acid in the malonic acid BZ system provides strong evidence that in the presence of oxybromine species the oxidation of the (very reactive) malonic acid is diverted from the path which normally is expected to occur[6] and indeed followed by the (much less reactive) methylmalonic acid system.[4]

The use of the NMR technique appears to be very suitable in making further kinetic investigations on probable intermediates in the malonic acid system (such as tartronic acid, glyoxalic acid, mesoxalic acid, etc.) in order to see which of the possible intermediates are reactive and which are not, indicating where in the path the diversion occurs. This will be the subject of a longer subsequent study.

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