

B. Neumann, S. C. Müller, M. J. B. Hauser, O. Steinbock, R. H. Simoyi, N. S. Dalal:
The Role of Oxygen in the Belousov-Zhabotinsky Reaction: Detection and Kinetics of
Radicals in the Oxidation of Malonic Acid by Cerium(IV)

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Abstract:

Rapid scan EPR spectroscopy combined with stopped-flow techniques was utilized to characterize the formation and measure the decay kinetics of the peroxodicarboxymethyl radical (MAOO \cdot) in the oxidation of malonic acid (MA) by Ce(IV) under oxygen. The MAOO \cdot is characterized by its g-value of 2.0150 ± 0.0002 , together with a proton hyperfine coupling of 4.4 ± 0.2 G. Measurements in deuterated solvents and reactants exhibit an expected unresolved singlet at essentially the same g-value, thus supporting the radical identification. The measured decay curve for MAOO \cdot consisted of two distinct regimes: a slow decrease, followed by a rapid exponential decay with $k_{\text{exp}} = 1.8 \text{ s}^{-1}$. Oxygen consumption measurements indicated that the change of regimes corresponds to switching from aerobic to anaerobic reaction kinetics. Numerical simulations based on a simple kinetic model agree well with the observed radical decay kinetics. These results appear to provide significant new clues to the role of oxygen in the presently studied subset of the Belousov-Zhabotinsky reaction.