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ENVIRONMENTAL SCIENCE ARCHIVES
ISSN: 2583-5092
Volume V Issue 2, 2026

SHORT COMMUNICATION OPEN ACCESS

Kinetics of Oxidation of Curcumin in Presence of Various Oxidizing Agents in Different Solvents

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Received: 2026/06/12
Accepted: 2026/07/28
Published: 2026/08/02

Abstract

Curcumin, the primary bioactive curcuminoid from *Curcuma longa*, displays potent antioxidant activity yet is highly susceptible to oxidation, impacting its stability, bioavailability, and utility in environmental applications such as pollutant scavenging and natural preservative systems. This review comprehensively examines kinetic studies on curcumin oxidation up to 2025, encompassing oxidants including hydrogen peroxide, peroxydisulfate, hypochlorite, transition metal ions, reactive oxygen species (ROS), and autoxidation across diverse solvents (aqueous buffers, ethanol, DMSO, acetonitrile, and lipid media). Predominantly first-order or pseudo-first-order kinetics are observed, with rate constants spanning several orders of magnitude depending on pH, solvent polarity, temperature, and oxidant type. Organic protic solvents generally confer greater stability compared to alkaline aqueous media. The review incorporates data tables, comparative graphs, and Arrhenius insights derived from primary literature. Environmental implications for green chemistry and gaps in real-matrix studies are highlighted.

Keywords: Curcumin; Solvent effects; Rate constants; Autoxidation; Hydrogen peroxide; Environmental stability; Degradation products

Introduction

Curcumin (1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione) is widely studied for its anti-inflammatory, antioxidant, and potential bioremediation properties. Its chemical instability, particularly via oxidation, limits practical applications. Oxidation pathways yield products such as bicyclopentadione, vanillin, ferulic acid, and feruloyl methane. Research evolved from early pH-dependent degradation studies in the 1980s to detailed kinetic investigations post-2010 incorporating various oxidants and solvents, driven by needs in food, pharmaceutical, and environmental sciences.

Structure and General Degradation Pathways

Curcumin exhibits keto-enol tautomerism, with the enol form predominant in most solvents, facilitating hydrogen atom transfer (HAT) or single-electron transfer (SET) during oxidation. Degradation is highly pH-dependent: relatively stable under acidic conditions (pH < 7) but rapidly degrades in neutral-to-alkaline media via autoxidation.

Autoxidation and pH Effects

Autoxidation in aqueous buffer at pH 8.0 follows first-order kinetics with a rate constant of approximately 280×10^{-3} h^{-1} ($t_{1/2} \approx 2.5$ h). Early work by Tønnesen et al. (1985) established pH-dependent degradation kinetics, with rates increasing sharply above neutral pH. Wang et al. (1997) reported ~90% degradation within 30 min in phosphate buffer (pH 7.2, 37°C).

Hydrogen Peroxide and Peroxo Compounds

Biomimetic oxidation with H_2O_2 catalyzed by iron porphyrins in dichloromethane has been detailed. Nanozyme studies with curcumin-stabilized gold nanoparticles show Michaelis-Menten kinetics for H_2O_2. Peroxydisulfate and related systems exhibit solvent-dependent photooxidation behavior.

Halogen Oxidants and Metal Ions

Hypochlorite (relevant to water treatment) induces rapid second-order oxidation. Transition metals (Cu^{2+}, Fe^{3+}) catalyze Fenton-like processes, with rates modulated by solvent dielectric.

Radical and DPPH Kinetics

Curcumin scavenges peroxyl radicals with high rate constants in lipid media. Foti et al. (2016) elucidated separated coupled proton-electron transfer in DPPH• reactions, with kinetics dependent on phenolic OH groups and solvent. Truong et al. (2025) reported HOO• scavenging: overall rate constants ~9.36×10^7 $M^{-1}s^{-1}$ in water for curcumin I, significantly lower in less polar solvents.

Table 1. Representative Rate Constants for Curcumin Oxidation/Degradation

Oxidant/System	Solvent/Medium	Conditions	k (approx.)	Order	Key Reference
Autoxidation	Aq. buffer	pH 8.0, 37°C	280×10^{-3} h^{-1}	1st	Naksuriya et al. (2016)
pH-dependent degradation	Phosphate buffer	pH 7.2, 37°C	Rapid (~90% in 30 min)	1st	Wang et al. (1997)
DPPH•	Ethanol	25°C	1.8×10^4 $Lit.Mol^{-1}s^{-1}$ (for curcumin)	Bi-exponential	Foti et al. (2016)
HOO•	Water	Theoretical/calc.	9.36×10^7 $Lit.Mol^{-1}s^{-1}$	Varied (PCET/SET)	Truong et al. (2025)
Thermal (dry)	Solid/turmeric powder	Varied temp.	First-order, Ea reduced by matrix	1st	Luo et al. (2026)
H_2O_2 (catalyzed)	Dichloromethane	Biomimetic	Catalyst-dependent	—	Bandyopadhyay et al. (2003)

Solvent Effects on Oxidation Kinetics

Solvent polarity, hydrogen-bonding capacity, and dielectric constant strongly influence mechanisms (HAT vs. SPLET vs. SET).

- **Aqueous/Alkaline**: Fastest degradation.
- **Ethanol/Methanol**: Enhanced stability via H-bonding.
- **Aprotic (DMSO, Acetonitrile)**: Altered pathways and rates.
- **Lipid/Non-polar**: Relevant for food and membrane models.

Mondal et al. (2016) highlighted solvent and salt effects on self-degradation.
Arrhenius analyses from thermal and solvent-varied studies show activation energies typically 50–150 kJ/mol, lower in protic media for certain processes.

Mechanistic Insights and Product Analysis

Primary mechanisms involve phenolic OH abstraction or central methylene attack, leading to quinone intermediates and cyclized products. DFT studies and pulse radiolysis support solvent-tuned reactivity.

Environmental Implications

In environmental contexts, curcumin's rapid aqueous oxidation suggests low persistence in water bodies but utility in controlled antioxidant or sensor applications. Oxidation products' eco-toxicity requires further assessment. Stabilized formulations (micelles, emulsions) extend utility in sustainable technologies.

Conclusion

Curcumin oxidation kinetics are highly condition-dependent, predominantly first-order, with solvent and pH as critical modulators. Organic media and encapsulation markedly improve stability.

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Author Contributions
RCS, ARSB and VS conceived the concept, wrote and approved the manuscript.

Acknowledgements
Not applicable.

Funding
Not applicable.

Availability of data and materials
Not applicable.

Competing interest
The authors declare no competing interests.

Ethics approval
Not applicable.

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Citation: Shekar RC, Sapuri-Butti AR and Srinivasulu V (2026) Kinetics of Oxidation of Curcumin in Presence of Various Oxidizing Agents in Different Solvents. Environmental Science Archives 5(2): 388-391.