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Inhibition by Free Radical Intermediates of the Autoxidation Reaction of Sulfur Dioxide in Atmosphere

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ABSTRACT: A free-radical reaction is any chemical reaction involving free radicals. This reaction type is abundant in organic reactions. Two pioneering studies into free radical reactions have been the discovery of the triphenylmethyl radical by Moses Gomberg (1900) and the lead-mirror experiment^[1] described by Friedrich Paneth in 1927. In this last experiment tetramethyllead is decomposed at elevated temperatures to methyl radicals and elemental lead in a quartz tube. The gaseous methyl radicals are moved to another part of the chamber in a carrier gas where they react with lead in a mirror film which slowly disappears.

When radical reactions are part of organic synthesis the radicals are often generated from radical initiators such as peroxides or azobis compounds. Many radical reactions are chain reactions with a chain initiation step, a chain propagation step and a chain termination step. Reaction inhibitors slow down a radical reaction and radical disproportionation is a competing reaction. Radical reactions occur frequently in the gas phase, are often initiated by light, are rarely acid or base catalyzed and are not dependent on polarity of the reaction medium.^[2] Reactions are also similar whether in the gas phase or solution phase.^[3]

KEYWORDS: free radical intermediates, autoxidation, sulfur dioxide, atmosphere, inhibition

I. INTRODUCTION

Autoxidation (sometimes auto-oxidation) refers to oxidations brought about by reactions with oxygen at normal temperatures, without the intervention of flame or electric spark.^[1] The term is usually used to describe the gradual degradation of organic compounds in air at ambient temperatures. Many common phenomena can be attributed to autoxidation, such as food going rancid,^[2] the 'drying' of varnishes and paints, and the perishing of rubber.^[3] It is also an important concept in both industrial chemistry and biology.^[4] Autoxidation is therefore a fairly broad term and can encompass examples of photooxygenation and catalytic oxidation^[1,2].

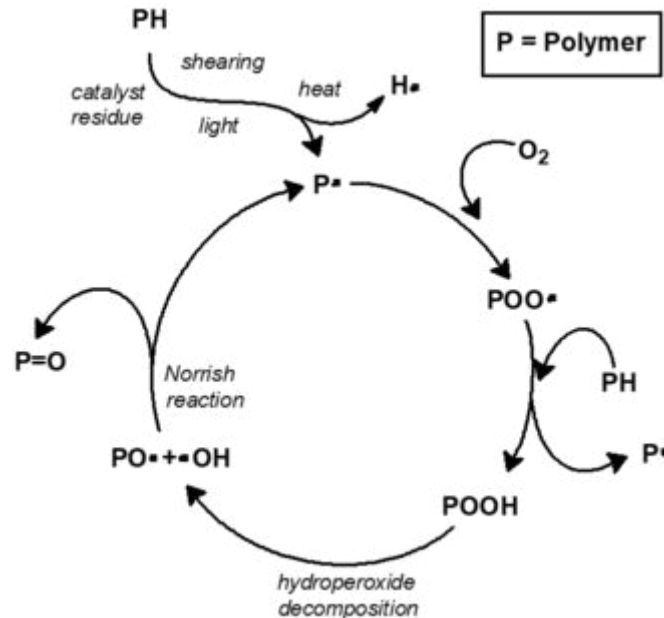
The common mechanism is a free radical chain reaction, where the addition of oxygen gives rise to hydroperoxides and their associated peroxy radicals (ROO•).^[5] Typically, an induction period is seen at the start where there is little activity; this is followed by a gradually accelerating take-up of oxygen, giving an autocatalytic reaction which can only be kept in check by the use of antioxidants. Unsaturated compounds are the most strongly effected but many organic materials will oxidise in this way given time.

Although autoxidation is usually undesirable it has been exploited in chemical synthesis. In these cases the term 'autoxidation' is often used more broadly to include spontaneous reactions with oxygen at elevated temperatures, such as in the Cumene process.

The free radical chain reaction is sometimes referred to as the Bolland-Gee mechanism^{[6][7]} or the basic autoxidation scheme (BAS)^[8] and was originally based on the oxidation of rubbers,^[9] but remains generally accurate for many materials. It can be divided into three stages: initiation, propagation, and termination.^[10] The initiation step is often ill-defined and many agents have been proposed as radical initiators.^[11] The autoxidation of unsaturated compounds may be initiated by reactions with singlet oxygen^[12] or environmental pollutants such as ozone and NO₂.^[13] Saturated polymers, such as polyolefins would be expected to resist autoxidation, however in practise they contain hydroperoxides formed by thermal oxidation during their high temperature moulding and casting, which can act as initiators.^{[14][15]} In biological systems reactive oxygen species are important. For industrial reactions a radical initiator, such as benzoyl peroxide, will be intentionally added.^[17,18]

All of these processes lead to the generation of carbon centred radicals on the polymer chain (R•), typically by abstraction of H from labile C-H bonds. Once the carbon-centred radical has formed, it reacts rapidly with O₂ to give a peroxy radical (ROO•). This in turn abstracts an H atom from a weak C-H bond give a hydroperoxide (ROOH) and a

fresh carbon-centred radical. The hydroperoxides can then undergo a number of possible homolytic reactions to generate more radicals,^[8] giving an accelerating reaction. As the concentration of radicals increases chain termination reactions become more important, these reduce the number of radicals by radical disproportionation or combination, leading to a sigmoid reaction plot.[19,20]



Cyclic mechanism of autoxidation

II. DISCUSSION

The autoxidation of unsaturated fatty acids causes them to crosslink to form polymers.^[16] This phenomenon has been known since antiquity and forms the basis of drying oils, which were traditionally used to make many varnishes and paints.^[17] Linseed oil, which is rich in polyunsaturated fats, is a prime example.[13,14]

Conversely, autoxidation can also cause polymers such as plastics to deteriorate.^[18] Sensitivity varies depending in the polymer backbone, in general structures containing unsaturated groups, allylic and benzylic C–H bonds and tertiary carbon centres are more susceptible, rubbers are therefore particularly sensitive. Autoxidation can be inhibited by a wide range of polymer stabilizers, or accelerated by biodegradable additives. Similarly, antioxidant oil additives and fuel additives are used to inhibit autoxidation.[3,4]

The prevention of autoxidation is important in the food and drink industry and is achieved both by both chemical preservatives and a range of oxygen excluding food preservation techniques such as canning. It is well known that fats, especially polyunsaturated fats, become rancid, even when kept at low temperatures,^[19] however many other foods are susceptible to autoxidation. The complex mixture of compounds found in wine, including polyphenols, polysaccharides, and proteins, can undergo autoxidation during the aging process, leading to wine faults. The browning of many foods, such as skinned apples, can be considered an autoxidation process, although it is generally an enzymatic process such as lipid peroxidation which proceeds via a different mechanism

In the chemical industry many chemicals are produced by autoxidation:

- in the cumene process phenol and acetone are made from benzene and propylene
- the autoxidation of cyclohexane yields cyclohexanol and cyclohexanone.^[20]
- p-xylene is oxidized to terephthalic acid
- ethylbenzene is oxidized to ethylbenzene hydroperoxide, an epoxidizing agent in the propylene oxide/styrene process POSM[11,12]
-



III. RESULTS

The fact that the thermal power and other plants continuously belch SO₂ and flyash concurrently made us to look into the chemistry of autoxidation of aqueous sulphur dioxide in aqueous suspensions of four different flyash samples obtained from three different thermal power and a fertilizer plants. The particle sizes and metal contents of each flyash sample were determined. Detailed kinetics investigation showed the major catalysis to be due to leached trace metal ions, and in agreement with the general rate law.[5,6]

where, $a \leq 0.5$; $b = 1.5-2$; $c = 0.4-1.5$

The atmospheric calculations indicated the conversion rates of around 0.34 to 1. "59% due to wetted flyash aerosols. Severe winter haze events in Beijing and North China Plain are characterized by rapid production of sulfate aerosols with unresolved mechanisms. Oxidation of SO₂ by O₂ in the absence of metal catalysts (uncatalyzed autoxidation) represents the most ubiquitous SO₂ conversion pathway in the atmosphere. However, this reaction has long been regarded as too slow to be atmospherically meaningful.[9,10] This traditional view was based on the kinetic studies conducted in bulk dilute solutions that mimic cloudwater but deviate from urban aerosols. Here, we directly measure the sulfate formation rate via uncatalyzed SO₂ autoxidation in single (NH₄)₂SO₄ microdroplets, by using an aerosol optical tweezer coupled with a cavity-enhanced Raman spectroscopy technique[15,16]. We find that the aqueous reaction of uncatalyzed SO₂ autoxidation is accelerated by two orders of magnitude at the high ionic strength (~36 molal) conditions in the supersaturated aerosol water. Furthermore, at acidic conditions (pH 3.5–4.5), uncatalyzed autoxidation predominately occurs on droplet surface, with a reaction rate unconstrained by SO₂ solubility. With these rate enhancements, we estimate that the uncatalyzed SO₂ autoxidation in aerosols can produce sulfate at a rate up to 0.20 μg m⁻³ hr⁻¹, under the winter air pollution condition in Beijing.

IV. CONCLUSIONS

S(IV) autoxidation by comparing the inhibiting activity of cis-verbenol (C₁₀H₁₅OH), myrtenol (C₁₀H₁₅OH) and nopol (C₁₁H₁₇OH) with that of ethanol (C₂H₅OH) and 2-propanol (C₃H₇OH). Results of laboratory experiments on the kinetics of S(IV) autoxidation in the presence of these alcohols were interpreted using the equation derived by Aleya and Bäckström, brought into relationship with the actual mechanistic knowledge on the reactivity of the inhibitors with respect to sulphate radicals. The rate constants for the reaction: $\text{alc} + \text{SO}_4^{\cdot-} + \text{O}_2 \rightarrow \text{SO}_4^{2-} + \text{H}^+ + \text{HO}_2 + \text{ald}$ involving cis-verbenol and myrtenol have been determined as equal to, respectively, 5.4×10^9 and $4.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. These results were obtained under the assumption that the main chain termination is due to simultaneous scavenging SO₅^{·-} radical anions by Fe^{II} and SO₄^{·-} radical anions by an alcohol. In the case of nopol the rough estimate gave for the rate constant of the latter reaction a value of $9.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ burdened with an error caused by the sulphony radical induced autoxidation of nopol. The studied airborne compounds of biological origin were shown to be potentially significant modifiers of the acidity formation in clouds and a sink for sulphony radicals participating in further transformations of these compounds.[7,8]

REFERENCES

1. Foote, Christopher S. (1996). "2. Autoxidation". Active Oxygen in Chemistry. Dordrecht: Springer Netherlands. pp. 24–65. ISBN 978-94-007-0874-7. doi:10.1007/978-94-007-0874-7_2
2. ^ Holman, Ralph T. (January 1954). "Autoxidation of fats and related substances". Progress in the Chemistry of Fats and Other Lipids. 2: 51–98. doi:10.1016/0079-6832(54)90004-X.
3. ^ Helberg, Julian; Pratt, Derek A. (2020). "Autoxidation vs. antioxidants – the fight for forever". Chemical Society Reviews. 50 (13): 7343–7358. doi:10.1039/D1CS00265A.
4. ^ Frank, Charles E. (February 1950). "Hydrocarbon Autoxidation". Chemical Reviews. 46 (1): 155–169. doi:10.1021/cr60143a003. PMID 24537520.
5. ^ Simic, Michael G. (February 1981). "Free radical mechanisms in autoxidation processes". Journal of Chemical Education. 58 (2): 125. Bibcode:1981JChEd..58..125S. doi:10.1021/ed058p125.
6. ^ Named after Geoffrey Gee and John Lawson Bolland
7. ^ Hammond, Earl G.; White, Pamela J. (July 2011). "A Brief History of Lipid Oxidation". Journal of the American Oil Chemists' Society. 88 (7): 891–897. doi:10.1007/s11746-011-1761-8. S2CID 84637577.
8. ^ Smith, Leesa M.; Aitken, Heather M.; Coote, Michelle L. (18 September 2018). "The Fate of the Peroxyl Radical in Autoxidation: How Does Polymer Degradation Really Occur?". Accounts of Chemical Research. 51 (9): 2006–2013. doi:10.1021/acs.accounts.8b00250. hdl:1885/209140. PMID 30016062. S2CID 51679950.



9. ^ Bolland, J. L.; Gee, Geoffrey (1946). "Kinetic studies in the chemistry of rubber and related materials. II. The kinetics of oxidation of unconjugated olefins". *Transactions of the Faraday Society*. 42: 236. doi:10.1039/TF9464200236.
10. ^ K. U. Ingold (1961). "Inhibition of the Autoxidation of Organic Substances in the Liquid Phase". *Chem. Rev.* 61 (6): 563–589. doi:10.1021/cr60214a002.
11. ^ Atmospheric oxidation and antioxidants. Amsterdam: Elsevier. 1993. ISBN 0-444-89615-5.
12. ^ Choe, Eunok; Min, David B. (September 2006). "Mechanisms and Factors for Edible Oil Oxidation". *Comprehensive Reviews in Food Science and Food Safety*. 5 (4): 169–186. doi:10.1111/j.1541-4337.2006.00009.x.
13. ^ "Initiation of the Autoxidation of Polyunsaturated Fatty Acids (PUFA) by Ozone and Nitrogen Dioxide". *Autoxidation in food and biological systems*. New York: Plenum Press. 1980. pp. 1–16. ISBN 978-1-4757-9351-2. doi:10.1007/978-1-4757-9351-2_1
14. ^ Grause, Guido; Chien, Mei-Fang; Inoue, Chihiro (November 2020). "Changes during the weathering of polyolefins". *Polymer Degradation and Stability*. 181: 109364. doi:10.1016/j.polydegradstab.2020.109364. S2CID 225243217.
15. ^ David, C. (1975). "Chapter 4 Oxidative Degradation of Polymers". *Degradation of polymers*. Amsterdam: Elsevier Scientific Pub. Co. pp. 425–538. ISBN 978-0-444-41155-6. doi:10.1016/S0069-8040(08)70336-4
16. ^ Wexler, Herman (1 December 1964). "Polymerization of Drying Oils". *Chemical Reviews*. 64 (6): 591–611. doi:10.1021/cr60232a001.
17. ^ Honzíček, Jan (17 July 2019). "Curing of Air-Drying Paints: A Critical Review". *Industrial & Engineering Chemistry Research*. 58 (28): 12485–12505. doi:10.1021/acs.iecr.9b02567. hdl:10195/74955.
18. ^ Grassie, Norman (1988) [1985]. *Polymer degradation & stabilisation* (1st pbk. ed.). Cambridge [England]: Cambridge University Press. ISBN 9780521357975.
19. ^ Prabhu, H. Ramachandra (August 2000). "Lipid peroxidation in culinary oils subjected to thermal stress". *Indian Journal of Clinical Biochemistry*. 15 (1): 1–5. doi:10.1007/BF02873539. PMC 3453543. PMID 23105229.
20. ^ I.V. Berezin, E.T. Denisov, *The Oxidation of Cyclohexane*, Pergamon Press, New York, 1996.



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