Fine organic synthesis using non-polluting and inexhaustible solar energy

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Abstract

In this study, our team conducted a comprehensive kinetic and mechanistic investigation to elucidate the interplay between pathways of aldehyde autoxidation. Subsequently, we established an efficient eco-friendly method to oxidize aldehydes to their corresponding peracids under sunlight or UV irradiation using oxygen as the sole oxidant without any additives or photocatalysts. Additionally, we demonstrated a simple method for aldehydes autoxidation to carboxylic acids *via* controlling key parameters such as the wavelength and solvent. These methods exhibit broad applicability to aromatic and aliphatic aldehydes, successful scaling up to the gram scale, and utilizing renewable solar energy making them good alternatives for traditional methods.

Background & Results

Approximately 5% of global carbon emissions are attributable to producing the chemicals that are essential to modern life. Creating a sustainable solution to one chemical reaction in particular - the autoxidation of aldehydes - has challenged researchers for decades due to the multiple pathways involved in this reaction. In this research, we have provided a solution to this problem (Figure 1). Through reaction kinetics and mathematical modelling, we studied the key details of autoxidation of aldehydes to peracids in various solvents, atmospheric conditions, and light sources. Peracids are incredibly useful because they can catalyze the conversion of a wide range of molecules by well-established chemistry. Unfortunately, the reaction conditions that are commonly used to produce peracids are wasteful, require dangerous additives, or have other fundamental complications. This time, optimizing the sustainability of the autoxidation of aldehydes was the goal of the research team's study. The researchers reported 18 examples of fast reactions of various aldehydes into peracids, in a pure oxygen atmosphere. These conditions suppressed further reaction to carboxylic acids. They furthermore reported 32 examples of slow reactions of various aldehydes into carboxylic acids through peracid intermediates, in a normal atmosphere. Some of these 50 reactions proceeded best under sunlight, or alternatively under an LED light. All reactions were at approximately room temperature, and in safe solvents. This work is the first time that peracids were synthesized from aldehydes using only sunlight and oxygen.

Significance of the research and Future perspective

This work is an important step forward in solving a previously vexing problem in peracid synthesis that has limited the environmental sustainability of producing such molecules. The optimized autoxidation reaction conditions identified in this study are applicable to a wide range of common chemical starting materials. Because the procedures are safe and cheap, practical applications in diverse syntheses should be straightforward. Our efforts have deduced the factors that underpin common oxidation of aldehydes in air, which has helped optimize the environmental sustainability of wasteful or even dangerous chemical synthesis.

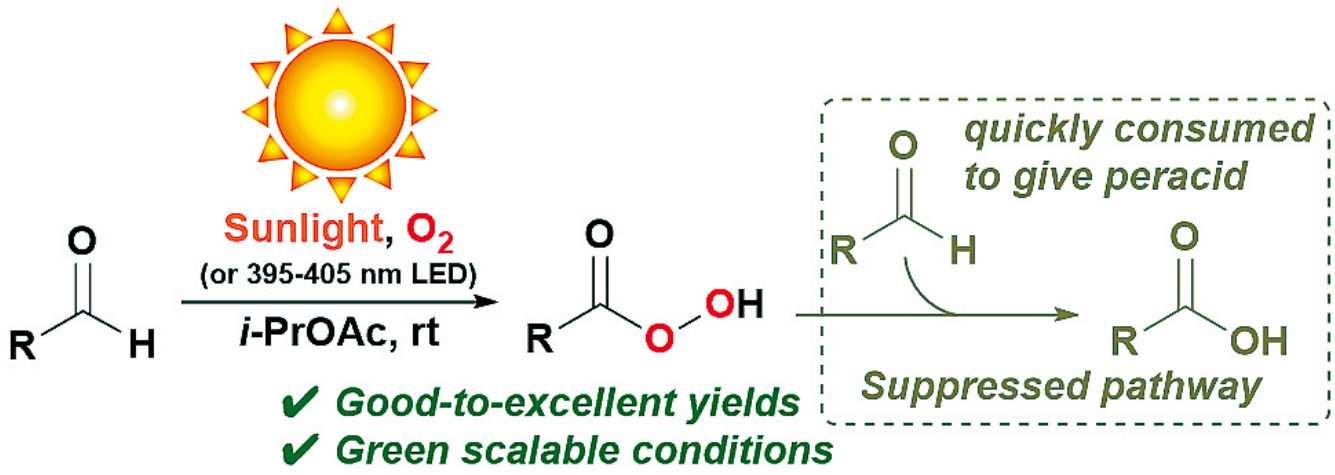

Figure 1

Patent	Japanese Patent Application No. 2023-192801
Treatise	Salem, Mohamed, S. H.; Takizawa, Shinobu; Kirihara, Masayuki et al. Light-induced autoxidation of aldehydes to peracids and carboxylic acids. Green Chemistry. 2024, 26(1), 375-383. doi: 10.1039/D3GC02951D Salem, Mohamed, S. H.; Takizawa, Shinobu; Kirihara, Masayuki et al. Green and efficient protocols for the synthesis of sulfonyl fluorides using potassium fluoride as the sole fluorine source. ACS Sustainable Chemistry & Engineering. 2024, 12(32), 12135-12142. doi: 10.1021/acssuschemeng.4c03951 Salem, Mohamed, S. H.; Khalid, Md, Imrul; Takizawa, Shinobu et al. Electrochemical synthesis of hetero[7]helicenes containing pyrrole and furan rings via an oxidative heterocoupling and dehydrative cyclization sequence. Advanced Synthesis & Catalysis. 2023, 365(3), 373-380. doi: 10.1002/adsc.202201262
URL	https://www.sanken.osaka-u.ac.jp/en/organization/srp/srp04.html
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