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Short communication: Reactivity of diacetyl with cleaning and sanitizing agents

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ABSTRACT

Diacetyl is used to impart a buttery flavor to numerous food products such as sour cream, cottage cheese, vegetable oil–based spreads, baked goods, and beverages. Recent studies have linked exposure to high concentrations of diacetyl and the onset of bronchiolitis obliterans. Due to the reported risks that diacetyl may pose, many food companies have altered practices to reduce worker exposure to diacetyl, including the use of personal respirators, improved air handling systems, and adequate cleaning practices. Commonly used cleaning and sanitizing agents may be reactive with diacetyl; however, the efficacy of these chemicals has not been studied in detail and remains unclear. The objective of this work was to study the reaction chemistry of diacetyl with common industrial cleaning and sanitizing chemicals. The reactions were assessed at equimolar concentrations and analyzed by gas chromatography-mass spectrometry. Peroxyacetic acid was most reactive with diacetyl (95% reduction in diacetyl), followed by sodium hypochlorite (76% reduction), and hydrogen peroxide (26% reduction). Benzalkonium chloride (BAC) did not react with diacetyl. Acetic acid was detected as the main product of reactions of diacetyl with peroxyacetic acid, sodium hypochlorite, and hydrogen peroxide. 1,1-Dichloro-2-propanone and 1,1,1-trichloropropanone were also identified as volatile reaction products in the sodium hypochlorite reactions.
Key words: diacetyl, cleaning chemical, carbonyl reactivity

Short Communication

Diacetyl is a commonly encountered aroma-active compound present in many food systems. Diacetyl has a distinctive buttery aroma and is commonly used to impart flavor to numerous food products such as sour cream, cottage cheese, baked goods, vegetable oil–based spreads, and beverages. Diacetyl is added to these products either alone or as part of complex flavoring mixtures.

Recent studies have found a direct correlation between exposure to high concentrations of diacetyl and the onset of bronchioloitis obliterans, a debilitating lung disease (Kreiss, 2007; van Rooy et al., 2007). Bronchioloitis obliterans is a rare, irreversible disease in which the formation of granular tissue obstructs the small airways, reducing lung capacity to the degree that a lung transplant may be required. Because of the reported risks that diacetyl may pose, many food companies have altered practices to reduce worker exposure to this chemical or have selected nondiacetyl-based flavorings that may include other vicinal dicarbonyl compounds, such as 2,3-pentanedione.

The US Occupational Health and Safety Administration (OSHA) has provided guidelines to limit worker exposure to diacetyl, including the use of personal respirators, adequate air handling systems, and adequate cleaning practices (OSHA, 2010). Diacetyl and its homologous replacements may be reactive with compounds common to industrial cleaning applications, such as halogen-containing agents, peroxide, or quaternary ammonium compounds.

The different oxidative capacities of these cleaning chemicals and the tendency of carbonyl groups to undergo nucleophilic addition reactions suggest that some of these chemicals may be more prone to react with diacetyl and other vicinal dicarbonyl compounds used as flavorants. It has been reported that α-diketones are oxidized by hydrogen peroxide (H_2O_2) or peroxyacids to the corresponding acid anhydrides (Figures 1 and 2; Cullis et al., 1987) following the epoxide mechanism or the Baeyer-Villiger (**BV**) reaction (Craig, 1999). The halogen-mediated oxidation of carbonyls to yield first trihalomethyl ketones and finally carboxylic acids (Lieben haloform reaction) is described in Figure 3 (Verter, 1970). The commonly used benzalkonium chloride (**BAC**) sanitizer is regarded as a surface-active chemical based on the positively charged nitrogen atom. However, its chemical reactivity in this realm has not been reported and it may not react with the carbonyl group. Effectively removing diacetyl from the processing environment and understanding the reactive

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fate of dicarbonyls is a critical component of reducing worker exposure. This work seeks to study the reactivity of diacetyl with 4 commonly used cleaning agents: H_2O_2, peroxyacetic acid (**PAA**), sodium hypochlorite (**NaOCl**), and BAC at equimolar ratios and to identify the volatile products of such reactions.

The study was conducted using authentic compounds of diacetyl (99%), NaOCl (10–15%), PAA (32%), BAC (95%), acetic acid (99%), acetic acid anhydride (99%), 1,1-dichloro-2-propanone (99%), and 1,1,1-trichloropropanone. All reagents were purchased from a single manufacturer (Sigma-Aldrich, St. Louis, MO) except H_2O_2 aqueous solution (30% in H_2O) and the HPLC-grade water used for dilution purposes (both from Fisher Scientific, Chicago, IL). Isopropyl alcohol (99%) was used as an internal standard (35 mmol; Sigma-Aldrich).

Aqueous solutions containing diacetyl (50 mmol) with equimolar concentrations (50 mmol) of each cleaning chemical in 10-mL glass vials (23 × 46 mm, 20-mm crimp) were hermetically crimped with an aluminum

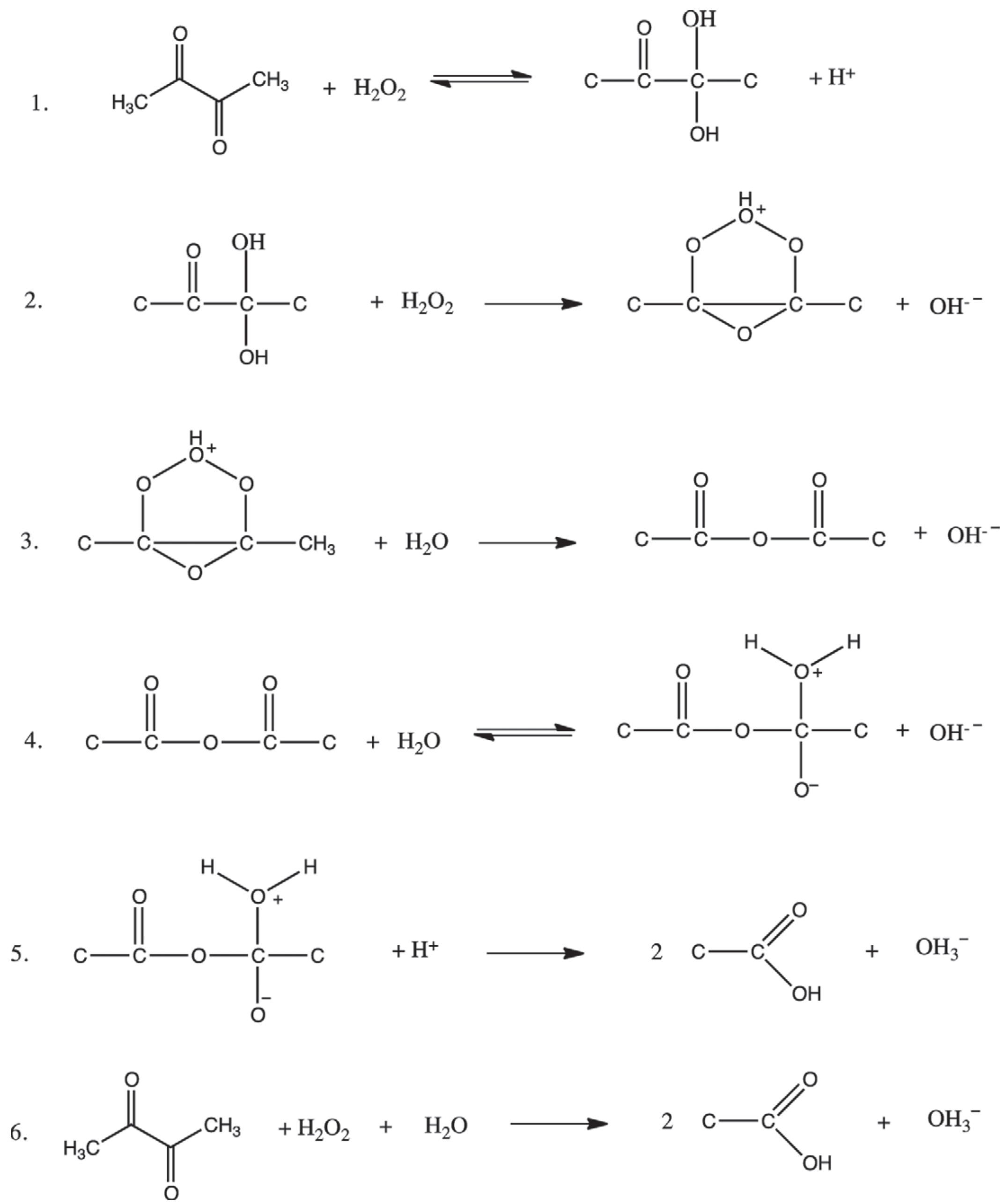

Figure 1. Reactions and stoichiometry of hydrogen peroxide with diacetyl (Frankvoort, 1978).