Intensified and safe ozonolysis of fatty acid methyl esters in liquid CO_2 in a continuous reactor

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Abstract

We demonstrate a continuous reactor for performing the ozonolysis of fatty acid methyl esters (FAMEs) using liquid CO_2 as solvent. The fast reaction kinetics allows the use of small-volume reactors to completely convert the FAMEs, forming secondary ozonides as the primary products. The short residence times also help maximize the yields of the secondary ozonides by minimizing over-oxidation and the formation of oligomeric products. The liquid CO_2 medium promotes safe reactor operation by providing an essential fraction of overall reactor cooling and by diluting the vapor phase organics. We also demonstrate a continuous stirred reactor for the safe thermal decomposition of the secondary ozonides to their corresponding acids and aldehydes. Using a lumped kinetic model for the thermal decomposition of the ozonolysis products, we estimate activation energy values of 108.6 ± 0.6 kJ mol^{-1} for the decomposition of secondary ozonides and 122 ± 3 kJ mol^{-1} for the decomposition of the undesired oligomeric species.

Keywords

Ozonolysis; Liquid CO_2; Fatty acid methyl esters; Continuous reactor; Secondary ozonide

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Introduction

Ozonolysis has long been of interest for the oxidative cleavage of double bonds to produce polymer precursors, pharmaceuticals, and other fine chemicals. For example, the ozonolyis of the unsaturated fatty acid methyl esters (FAMEs) in biodiesel and in vegetable oils is capable of producing a range of value-added acids and aldehydes with chain lengths ranging from C_3 to C_{13}. Such alternate technologies for the production of renewable industrial chemicals have the potential to improve biorefinery economics, for example, by diverting part of the biodiesel as feedstocks to produce chemicals with more value than the fuel itself. Feedstocks from renewable sources are also gaining increased importance as a result of depleting petroleum feedstocks and their unpredictable price fluctuations. New chemical technologies that can be easily integrated into the existing distributed biorefineries through modularization (i.e., without the need for large-scale reactors) are particularly desirable. A continuous ozonolysis concept aligns itself with the distributed biorefinery concept given that ozone is readily produced from air and that the ozonolysis of FAMES in liquid CO_2 occurs rapidly.[1-3] In addition to biorefining, ozonolysis has also attracted interest in pharmaceutical processing since ozone does not suffer from waste disposal issues associated with toxic oxidants such as osmium tetroxide.[4]

Ozonolysis, however, must be conducted safely as the intermediates and by-products of ozonolysis can spontaneously undergo exothermic decomposition, often leading to thermal runaway conditions. Additionally, the instability and explosive nature of pure ozone necessitate its use in significantly diluted form (<11%) in either the air or pure oxygen from which it is generated. These risks often pose a challenge to conduct ozonolysis even at laboratory scales. However, many of these risks can be mitigated with reliable knowledge of the reaction chemistry, proper solvent selection and rational reactor/process design to prevent runaway conditions (i.e., inherently safe design). Such an approach is not different to that adopted for the safe industrial practice of exothermic oxidation processes such as ethylene epoxidation.

The ozonolysis of methyl oleate, a fatty acid methyl ester (FAME), is practiced industrially via the so-called Emery process.[5] This process uses one of the reaction products, nonanoic acid, as a solvent to reduce the viscosity of the reaction mixture and thereby to enhance ozone transfer rates into the liquid phase. In addition, the nonanoic acid also participates in the reaction generating carboxy hydroperoxides as intermediates as opposed to the secondary ozonides that result from conventional ozonolysis. However, such a pathway is specific to feedstocks for which organic acids are produced as the desired products. Conventional solvents used for ozonolysis chemistry tend to be either halogenated hydrocarbons (e.g. CCl_4, $CHCl_3$, or CH_2Cl_2) or water due to their oxidation resistance. The toxicity and environmental concerns associated with halogenated solvents make them undesirable. Even though water is considered a benign solvent, water participates in ozonation by producing hydroxyl radicals that result in the complete, rather than selective, oxidation of organic compounds via advanced oxidation processes (AOPs).[6] It is for this reason that ozone is often used for municipal water purification.

Recently, we demonstrated the use of liquid CO_2 as an ideal and environmentally benign solvent for ozonolysis.[7] Liquid CO_2 is inexpensive, abundantly available and inert to ozone, thereby avoiding free radical chemistry that leads to non-selective products. Intrinsic solubility studies revealed that at subambient temperatures (-2 to 10°C), ozone is stable in liquid CO_2 and also significantly more soluble than it is in chlorinated solvents such as CCl_4. In batch reactor studies, rapid and highly selective ozonolysis of methyl oleate to ozonides and oligomeric products was demonstrated in liquid CO_2. In addition, the presence of dense CO_2 in the gas phase (65-68 mol %) helps to either significantly shrink if not eliminate the flammability envelope.[8]

The successful demonstration of rapid batch ozonolysis in liquid CO_2 led us to explore the development of a continuous ozonolysis process. Continuous ozonolysis processes have been reported in the literature,[4,9-12] mostly demonstrated with conventional solvent media. For enhancing process safety, microchannel reactors with reduced residence time, minimal holdup of reactants and high surface areas have been used.[11-14] We report herein the first successful demonstration of continuous ozonolysis with liquid CO_2 as the medium. To accomplish this, previously reported intrinsic solubility data for ozone in liquid CO_2 along with demonstration of the nearly stoichiometric reaction of ozone with methyl oleate to produce the ozonolysis products[7] provided valuable guidance. While the increased albeit mild pressures (tens of bars) required for liquid CO_2-based ozonolysis increase capital equipment costs and compression energy requirements, product separation from liquid CO_2 is easily achieved by pressure reduction. We also demonstrate that the products obtained from the continuous ozonolysis of FAMEs (secondary ozonides) can be easily converted to acids and aldehydes by simple thermal decomposition in a continuous stirred reactor.

Materials & Methods

Ozonolysis reactor

The design of the continuous reactor is based on the experimental setup previously used to determine Henry's law coefficient for ozone in liquid CO_2.[7] A schematic of the laboratory reactor used for continuous ozonolysis of FAMEs is shown in Figure 1.

Ozone is generated from extra dry oxygen (99.6%, dew point < -50 °C, supplied by Matheson) by a Praxair-Trailigaz Unizone LO ozone generator and is temporarily held in a 300 ml 316 stainless steel pressure vessel. The majority of this ozone is fed to a compressor, while the remainder is vented after being routed through an ozone destructor. The compressor used is a RIX Microboost oxygen compressor retrofitted in-house for ozone compatibility with 316 SS and Kalrez® perfluoroelastomer components to tolerate high ozone concentrations and cooled to minimize adverse impacts of heat buildup on ozone stability. The compressed oxygen/ozone mixture is pumped to a high pressure reservoir before being fed into the reactor by a Brooks SLA mass flow controller. Any excess O_3/O_2 mixture is vented through a back pressure regulator to the ozone destruction unit after passing through a Teledyne API model 452 ozone analyzer, the data obtained from which is used to determine the quality of ozone feed to the reactor. Liquid CO_2 pumped by a Teledyne ISCO 500D dual syringe pump is mixed with the ozone/oxygen mixture entering the reactor via an Omega FMX 8400 series static mixer. Using the Henry's law coefficient of 0.23 mol bar^{-1} l^{-1} for O_3 in liquid CO_2,[7] an operating pressure of 70 bar and an ozone concentration of 4 mol% in the O_2/O_3 feed, it was estimated that 9.1 ml $CO_{2(l)}$ would be required to sequester the O_3 necessary for stoichiometric conversion of 1 ml of methyl oleate. Downstream of the static mixer, the substrate is pumped into the reactor via an additional ISCO pump and contacted with the O_3 rich liquid CO_2 at a simple mixing point. The resulting gas/liquid stream is directed to a high-pressure view cell where the gas and liquid phases are allowed to separate by gravity. The gas exits through a back pressure regulator to a second Teledyne API model 452 ozone analyzer and then an ozone destruction unit before being vented. Part of the liquid phase in the view cell is recycled back to the mixing point (to promote mixing) and a part is removed (to maintain a constant liquid level in the view-cell) and collected as product, with a recycle ratio held constant at 25:1 (volumetric recycle flow rate: volumetric product flow rate) by varying the speed of the gear pump. The reaction product is isolated by flashing off the CO_2 using pressure reduction.

A second configuration of the reactor with no recycle was also implemented. Without recycle, the type 316 SS tubing [25 cm long, 1/8" (3.175 mm) OD, 0.035" (0.889 mm) wall thickness with an effective volume of approximately 0.6 ml] from the mixing point to the view cell acted as the reactor with the view cell used to separate the vapor and liquid phases. With recycle, the addition of a gear pump and accompanying tubing led to a total volume of 14.5 ml which increased the residence time by more than 24-fold. As discussed later, increased residence times result in less desirable ozonolyis product distributions.

Reactor pressure is measured using Omega PX329 series pressure transducers and temperatures are measured with Omega HTQ series type T thermocouples. The reactor cooling to maintain temperature is provided by three sources: the feed stream, evaporation of liquid CO_2 in the reactor and an external chiller. The external chiller was used to provide the cooling needed for temperature control of the reactor, lines, and other devices such as the pumps. All data were recorded every 5 seconds by a National Instruments FieldPoint data acquisition system (DAQ) and a suitably interfaced computer.

Startup of the ozonolysis reactor was achieved by first chilling the reactor to the typical operating temperature of 0 °C before introducing liquid CO_2. After the liquid CO_2 level had stabilized, compressed O_3 was gradually introduced with the feed rate ramped up to the steady state flow-rate of 2000 std. ml min^{-1}. Following reactor pressurization to the operating pressure of 70 bar, additional CO_2 was added as necessary to maintain a constant liquid level. Upon achieving the desired operating temperature and pressure, control of the feed flow rates was switched from manual control to automatic. The flow-rates of the reactants are controlled based on user input of the desired FAME/O_3 ratio, FAME feed rate and the iodine number of the FAMEs being reacted. The iodine number provides a measure of the degree of unsaturation in a FAME mixture, and provides guidance to estimate the O_3 necessary to completely oxidize all double bonds. The mass flow rate of O_2/O_3 fed to the reactor (controlled by a Brooks MFC) is calculated based on the desired FAME/O_3 ratio and the concentration of ozone in the feed gas (measured by the ozone analyzer). Given that the concentration of O_3 produced by the generator varied between 3.7-4.3 mol%, it was necessary to independently control the substrate feed rate based on measurement of the O_3 concentration exiting the compressor to maintain a constant FAME/O_3 ratio in the feed. The manner in which the FAMEs are initially added to the reactor is dependent on the reactor configuration. When operating in the recycle mode, a substantial volume of O_3-saturated liquid CO_2 is present in the reactor prior to the introduction of FAMEs. Hence, the FAME stream was initially introduced at a rate of 5 ml min^{-1} for 20 s in order to consume the O_3 as completely as possible (to prevent over-oxidation of products) following which the FAME feed rate was reduced to the steady feed rate (typically ~1 ml min^{-1}) required to match the O_3 feed rate at the desired O_3/FAME ratio. In the configuration without recycle, substantially less O_3 was initially present in the reactor. Hence, the FAME feed rate was maintained at the predetermined steady state value from the start.

The excess O_3 and O_2 gases that are not absorbed in liquid CO_2 pass through the reactor in the vapor phase. The O_3 in the vapor phase continues to react with unreacted FAME solution and products in the liquid phase. In addition, the vapor phase also contains CO_2 that is continuously stripped from the liquid phase by the gas stream passing through the reactor. Vapor-liquid equilibrium modeling of the CO_2+O_2 binary system is used to estimate the amount of CO_2 stripped from the liquid phase at the system temperatures and pressures, and to estimate the required makeup CO_2 flow rates at steady state. [15] When the system pressure and temperature deviate from the preset ranges of operating pressure and temperature, a control program automatically initiates a safe reactor shutdown sequence.

Thermal decomposition reactor

The thermal decomposition of secondary ozonides (SOZs) obtained from the ozonolysis of FAMEs was performed in a stirred titanium Parr reactor with a total volume of 50 ml (Figure 2). Reactor startup was performed with nonanoic acid to allow the flow-rates and temperatures to stabilize before the ozonolysis product mixture containing SOZs was introduced. The neat SOZs-containing stream was pumped using an HPLC pump. Nitrogen gas, metered through a rotameter, was used to purge the headspace and maintain an inert blanket over the liquid phase in the reactor. The reactor was operated at atmospheric pressure. The dip tube insertion depth was adjusted to maintain steady holdup of the liquid phase at a predetermined volume of 14.2 ml and thereby maintain a constant liquid level in the reactor. The gas and the liquid phases flow through the dip-tube in a two-phase bubbly flow. The liquid/gas mixture exiting the dip tube was directed to a cooled container where the liquid product was separated and collected. The N_2 and any generated gas were allowed to escape via a fume hood. Decomposition temperatures ranging from 80 °C to 150°C were investigated. An SOZ feed rate of 0.71

ml min^{-1} was used to establish an average residence time of 20 min. Liquid products collected in the effluent stream over 10 min durations were analyzed by GC-MS and NMR.

Analytical methods

Starting materials and product solutions were analyzed by GC-MS and GC-FID by diluting 2 µl of recovered product with 1 ml of hexane. The GC method uses an HP-INNOWAX column in an Agilent 7890A GC coupled to a 5975C MS. A carrier gas flow of 1 std. ml min^{-1}, an inlet temperature of 250 °C and an injection volume of 1 µl were used. The oven temperature was initially held at 40 °C for 5 minutes, then ramped at 10 °C per minute to 220 °C and held at this temperature for a further 20 minutes. Masses were scanned from 20 to 500 Da.

The starting mixture and recovered products were also analyzed by NMR on a Bruker Avance III 500 MHz instrument at 25.0±0.1 °C equipped with a ^{13}C-observe cryoprobe (CPDUL) using the procedure described previously.[7] Quantitative ^{13}C spectra were obtained using 90° pulses and inverse-gated decoupling, with recycle delays set to $\geq 5T_1$ (60s) of the resonances of interest. Baselines were sparingly corrected using the Bernstein polynomial method in MestReNova. Using samples prepared with CD_2Cl_2, reference spectra were obtained with respect to residual protonated solvent.

The exact structure of the SOZ-like oligomeric (SOZLO) species that form alongside SOZs could not be determined. Further, with an unknown number of identical carbon atoms, the absolute concentration for SOZLOs is not quantifiable by ^{13}C-NMR. However, the concentration of SOZLOs is estimated on a relative basis by assuming that a T_1 relaxation time of 60 sec (as employed) is sufficient for quantification and that each non-SOZ carbon detected in the 99-111 ppm region of NMR spectra represents an oxidized carbon originating from a cleaved unsaturated double bond which has an average molecular weight of 172 (i.e., half of the molecular weight of methyl oleate SOZ, 344).

Results and Discussion

Continuous Ozonolysis of FAMEs

For both reactor modes, with and without recycle, a steady state product distribution was achieved within 6 minutes from startup. When the ozone was fed in stoichiometric excess (O_3/methyl oleate = 1.1), near total methyl oleate conversion was achieved during continuous ozonolysis. Steady state runs up to 240 minutes in duration have been demonstrated. At longer durations, managing the heat produced by the ozone compressor becomes important. The compressor must be sufficiently cooled to prevent ozone decomposition.

Table 1 summarizes representative results from two experiments, with and without recycle of the reactor liquid phase. As described earlier, operation without recycle decreased the residence time, which prevents a large portion of the SOZs from being converted to various oligomeric byproducts (SOZLO)- as was observed when operating the reactor with recycle. Figure 3 shows a comparison of the region in the ^{13}C-NMR spectra associated with SOZs and SOZ-like oligomers (SOZLOs) (99-111 ppm), when the reactor is operated with and without the recycle stream.

Figure 4 shows the temporal product profiles during continuous ozonolyis without recycle. Almost complete conversion of methyl oleate and nearly steady product distribution are achieved in approximately six minutes. At steady state, more than 94 wt.% of C in the feed (on a CO_2-free basis) is accounted for in the products. The yield of SOZs is greater than 75%, with the SOZLOs constituting 10 wt.% of the reaction mixture. The remaining products are mostly C_9 acids and aldehydes, the desired products.

In an attempt to minimize CO_2 use to improve process economics, the CO_2/FAME ratio was reduced from 9.1 to 1.2 (at a fixed O_3/FAME ratio of 1.1) over the course of several experiments. In all cases, the steady state methyl oleate conversion was 99+%, with the mass production rate of the ozonized products equaling the FAME and O_3 addition rates. Liquid CO_2 acts as an effective carrier for O_3 and provides part of the cooling (by evaporation) to maintain the reaction temperature. The high vapor pressure of liquid CO_2 also helps to lower the concentrations of organic vapors in the oxygen-rich vapor phase. The heat balance in the reactor may be qualitatively described as follows. For steady reactor operation, the heat generation rate must be balanced by the heat removal rate. Given that the FAMEs are rapidly converted by the ozonolysis reaction, the heat generation rate is dictated by the FAME addition rate. The heat removal rate consists of three essential sources: (1) external cooing provided by a chiller; (2) the feed flow-rate consisting of the liquid CO_2 and FAMEs; and (3) evaporative cooling by CO_2. Uncompensated removal of any one of these sources can lead to thermal runaway due to the highly exothermic decomposition of the SOZLOs. This is the reason why a certain amount of liquid CO_2 must always be used in the feed. Hence, further reduction in the CO_2/FAME ratio below 1.2 was not attempted.

Using reactor operation with recycle, experiments were performed by varying the O_3/FAME ratio from 0.8 (i.e., O_3 is the limiting reagent) to 3 (substantial O_3 excess). The results are summarized in Table 2. It is clear from the product distribution in Table 2, that the SOZs undergo further reaction when exposed to increasing amounts of excess O_3 resulting in a significant loss of product selectivity. While the SOZ selectivity at a O_3/FAME ratio of 1.25 is approximately 25.2% (see Table 2), the selectivity increases to 75.4% when using a small-volume single-pass reactor. This further confirms that minimizing residence time is essential to avoid secondary reactions.

Thermal decomposition of secondary ozonides

Several attempts at performing thermal decomposition of the SOZs batch in a sealed batch reactor resulted in thermal runaway leading to undesired pressure spikes and product degradation. Further attempts to avoid thermal runaway while performing thermal decomposition in the batch reactor were unreliable and often futile despite the use of slow temperature ramps and inert gas blankets of either CO_2 or N_2. A tubular reactor was constructed in order to achieve better control of the heating, the concentration of the SOZs and the residence time to achieve controlled decomposition without thermal runaway. However, dissolved gases (primarily CO_2 from the ozonolysis reaction) in the reaction mixture generated a gaseous phase at the temperatures required for thermal decomposition resulting in a mixed gas/liquid slug flow that was unsuitable for obtaining kinetic data. Hence, the CSTR configuration described earlier was used to overcome this drawback and obtain data that are better suited for kinetic analysis.

The CSTR startup was performed with nonanoic acid, a product of the decomposition of the ozonized products, as solvent. The use of nonanoic acid as solvent serves to both lower the concentration of the SOZs entering the reactor (and thus the rate of heat generation upon decomposition) as well as to provide an inert heat sink to effectively absorb the heat of reaction and prevent thermal runaway conditions. Following establishment of a steady flow of ozonized products into the reactor, a steady state temperature was achieved in the CSTR within approximately one residence time (~20 min). GC and NMR analysis of products indicated that steady concentrations were typically achieved within three residence times. Experiments were performed for five residence times to ensure that samples with steady composition had been acquired.

The ^{13}C NMR analysis results from the thermal decomposition of the methyl oleate ozonolysis products at 115 °C are shown in Figure 5. The feed is from a continuous ozonolysis run with recycle as indicated by the dominant presence of SOZLOs in the mixture. The formation of acids and aldehydes significantly increases upon thermal decomposition of the SOZ and SOZLOs; however, the fraction of indeterminable species also increases with temperature resulting in a loss of yield of the desired products. A key challenge is to minimize the formation of undesired thermal decomposition products.

Further investigations reveal that there is a relationship between the decomposition temperature and the product yield from the SOZLO component of the feed mixture. When the ozonolysis product mixture is analyzed with a GC using an injection temperature of 250 °C, the only peaks that were consistently obtained are those of the four final products expected from the ozonolysis of methyl oleate: nonanoic acid; nonanal; nonanoic acid,9-oxo, methyl ester; and nonanedioic acid, monomethyl ester. Because the SOZs and SOZLOs are unstable at the temperature of the GC inlet, we hypothesize that all SOZs and SOZLOs are thermally decomposed in the GC injector. By comparing the GC/FID analysis and ^{13}C NMR analysis of the ozonolysis product mixture, we observed that the product concentrations obtained from GC/FID analysis stoichiometrically matched the concentrations of SOZs obtained by NMR analysis, excluding the SOZLO material. We conclude, therefore, that the indeterminable thermal decomposition products (see Figure 5) originate from the SOZLO material. This is also confirmed by Figure 6 that shows the yield of the desired thermal decomposition products obtained from the SOZLOs at the various temperatures. While higher temperatures dramatically increase the rate of decomposition of the SOZLOs, they significantly decrease the yield of the desired products (aldehydes and acids). To maximize the yield of the desired products, it is therefore essential to minimize the formation of SOZLOs (by minimizing residence times in the ozonolysis step) *and* to use lower decomposition temperatures.

Lumped kinetic model

Even though the thermal decomposition of the SOZs and SOZLOs yield an array of products, we employed a lumped kinetic modeling approach to obtain kinetic parameters to guide the rational operation and design of the exothermic thermal decomposition reactor (roughly 0.8±0.1 kJ g^{-1} based on a Parr 6200 Ioperibol Bomb Calorimeter measurement). Such an approach had been used effectively to model cracking reaction in the petroleum processing industry. To this end, we assume that the thermal decomposition reactions involving the SOZs and the SOZLOs occur via parallel independent pathways. Each such pathway is approximated as a lumped first order reaction system of the type, $A_i \rightarrow$ products, where A_1 represents the SOZs and A_2 represents the SOZLOs. This assumption allows the rate constants (k_1 for SOZs *and* k_2 for SOZLOs*)* at a given temperature to be determined from a steady state CSTR material balance equation by knowing only the substrate conversions (X_1 *and* X_2) and the mean residence time (τ) based on the liquid feed rate (Eq. 1).[16]

$$k_i = \frac{X_i}{\tau(1 - X_i)} \tag{1}$$

Figure 7 shows an Arrhenius plot, with rate constants (k_1 and k_2) at temperatures ranging from 80 °C to 150 °C. Excellent fits are observed (Figure 7), with an activation energy of 108.6±0.6 kJ mol^{-1} for the SOZs and a pre-exponential constant of 1.019 x10^{13} min^{-1}. As previously described, SOZLOs can only be quantified on a relative basis, which is adequate for this analysis because the conversion of SOZLOs is determined by their final and initial concentrations in the reactor feed and effluent. The kinetic analysis based on the assumptions described in analytical methods yields an activation energy of 122 ± 3 kJ mol^{-1} and a pre-exponential constant of 3.53 x10^{15} min^{-1} for the thermal decomposition of the SOZLOs (Figure 7).

Conclusions

Continuous ozonolysis of methyl oleate, a model FAME compound, was successfully demonstrated for the first time using liquid CO_2 as a solvent. With liquid CO_2 used as the solvent, the ozonolysis rates were immeasurably fast even when operating at maximum flow-rates and with minimum reactor volume. The presence of liquid CO_2 facilitates safe operation by providing some cooling due to the evaporation of liquid CO_2 during reaction and by diluting organic and oxygen content in the vapor phase. The primary products obtained from the ozonolysis of methyl oleate are primarily secondary ozonides and related oligomers, with some acids and aldehydes resulting from the decomposition of these intermediates. The yield of the secondary ozonides is maximized at shorter reactor residence times by preventing over-oxidation that results in the increased formation of oligomeric products.

The thermal decomposition of the secondary ozonides in nonanoic acid in a stirred reactor exclusively yields the desired aldehydes and acids over a wide temperature range. In contrast, the oligomeric species favor these desired products only at lower decomposition temperatures. In order to maximize the desired products, it is thus essential to minimize the formation of the oligomeric materials during the ozonolysis step. To guide the safe reactor operation and design, kinetic parameters were estimated for the exothermic thermal decomposition of both the secondary ozonides as well as the oligomeric species. Our results show that ozonolysis in liquid CO_2 has excellent potential for implementation in existing biodiesel plants as modular reactor units to achieve product diversification.

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