JACS Au
AN OPEN ACCESS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Facile Ozonation of Light Alkanes to Oxygenates with High Atom Economy in Tunable Condensed Phase at Ambient Temperature

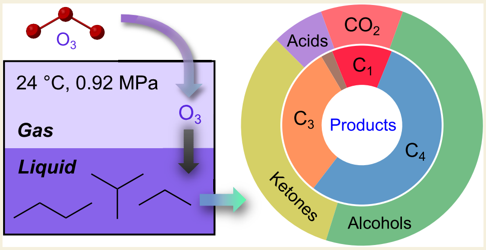
Hongda Zhu, Timothy A. Jackson, and Bala Subramaniam*

Cite This: *JACS Au* 2023, 3, 498−507

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: We have demonstrated the oxidation of mixed alkanes (propane, *n*-butane, and isobutane) by ozone in a condensed phase at ambient temperature and mild pressures (up to 1.3 MPa). Oxygenated products such as alcohols and ketones are formed with a combined molar selectivity of >90%. The ozone and dioxygen partial pressures are controlled such that the gas phase is always outside the flammability envelope. Because the alkane−ozone reaction predominantly occurs in the condensed phase, we are able to harness the unique tunability of ozone concentrations in hydrocarbon-rich liquid phases for facile activation of the light alkanes while also avoiding over-oxidation of the products. Further, adding isobutane and water to the mixed alkane feed significantly enhances ozone utilization and the oxygenate yields. The ability to tune the composition of the condensed media by incorporating liquid additives to direct selectivity is a key to achieving high carbon atom economy, which cannot be achieved in gas-phase ozonations. Even in the liquid phase, without added isobutane and water, combustion products dominate during neat propane ozonation, with CO_2 selectivity being >60%. In contrast, ozonation of a propane+isobutane+water mixture suppresses CO_2 formation to 15% and nearly doubles the yield of isopropanol. A kinetic model based on the formation of a hydrotrioxide intermediate can adequately explain the yields of the observed isobutane ozonation products. Estimated rate constants for the formation of oxygenates suggest that the demonstrated concept has promise for facile and atom-economic conversion of natural gas liquids to valuable oxygenates and broader applications associated with C−H functionalization.



KEYWORDS: *propane, isobutane, n-butane, mixed light alkanes, ozone, oxygenated products*

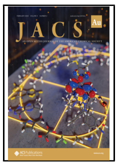
■ INTRODUCTION

Light alkanes such as ethane, propane, butanes, and pentanes are collateral products of shale gas extraction. The increased production of shale gas in the United States makes these hydrocarbons relatively inexpensive feedstocks for making value-added chemicals as opposed to being either flared or burned as fuel, both of which result in greenhouse gas emissions. Chemical and biochemical strategies to upgrade shale gas have been emerging,[1−6] including a two-step catalytic process of alkane dehydrogenation and oligomerization. The process was shown to be potentially more energy-efficient compared to the existing technology to produce fuels from natural gas liquids (NGLs).[6−8] Further, since shale gas reserves are widely distributed and often occur in remote locations, liquid products such as alkene oligomers could be easily transported to other locations, and thus potentially reduce transportation-related emissions.

The oxidative conversion of NGLs to oxygenates is also a promising route, as the oxygenates, including alcohols, are as easily transported as the oligomers. Producing alkenes by alcohol dehydration is another advantage of this route. For example, propylene can be accessed from isopropyl alcohol by dehydration catalyzed by acid catalysts.[9−11] The dehydration route is significantly less energy-intensive, requiring temperatures at least 200 °C lower compared to direct alkane dehydrogenation.[12−14]

Nonetheless, despite extensive research efforts, oxidative activation of C−H bonds by sustainable methods remains a grand challenge.[15−24] Not only are the alkanes recalcitrant to oxidation due to their high C−H bond dissociation energies of 330−460 kJ/mol,[15] but their alcohol and ketone oxygenates are also easier to oxidize. Thus, high oxygenate yields with low combustion product formation are often elusive.[15−18] The temperatures required for the activation of some components of NGLs by dioxygen are usually higher than the critical temperatures of ethane (32.1 °C) and propane (96.7 °C).[25] This means that aerobic oxidation can only be performed in the gas phase, and advantages of condensed phase oxidation, such as of higher substrate concentrations and tunable oxidant concentrations,[26] are lost.

Received: November 17, 2022
Revised: January 7, 2023
Accepted: January 18, 2023
Published: February 7, 2023



https://doi.org/10.1021/jacsau.2c00631

In contrast, the ozonation of alkanes has been reported at lower and even sub-ambient temperatures compared to those for oxidation with dioxygen.[27−45] Ozone readily oxidizes propane, *n*-butane, and isobutane in the gas phase at 50 °C and ambient pressure. Isobutane is oxidized to *tert*-butyl alcohol at ∼50% selectivity with a CO_2 selectivity of ∼16%.[27] However, gas-phase ozonation of the less reactive linear alkanes, propane, and *n*-butane, leads to over-oxidized C_1 products, including 55−78% CO_2.[27,28] Some early research used flammable mixtures of alkane and oxygen that favor combustion kinetically and thermodynamically. Further, at ambient temperatures, gas-phase ozonation is generally slow due to low substrate concentrations compared to liquid phase. Thus, elevated temperatures are often needed to promote initiation even in the presence of ozone, while a very short contact time is needed to restrict over-oxidation of intermediate oxidation products.[39,44−46] However, higher temperatures not only result in ozone decomposition but may also aid the formation of free radicals that promote C−C bond scission.

Liquid-phase ozonation in the presence of a solvent poses additional challenges. Ozone attacks most organic solvents more readily than it activates alkanes, which adversely affects the efficient utilization of ozone. Solvents such as chlorocarbons[47−49] and fluorocarbons[50−52] display enhanced resistance to ozone. However, these solvents pose environmental concerns.[53,54] While acetic acid can serve as a more environmentally benign solvent that is resistant to ozone oxidation, this solvent acts as a radical scavenger and thus does not act as an innocent solvent.[55] Liquid CO_2 ($P_c = 7.38$ MPa, $T_c = 31.1$ °C) is an excellent solvent for ozone.[56,57] Not only is CO_2 resistant to ozone attack but ozone is also highly soluble in liquid CO_2. The Henry's law constant for ozone in liquid CO_2 is approximately 0.25 $mol{\cdot}L^{-1}{\cdot}bar^{-1}$ in the temperature range of −10 to 4 °C.[57] This compares with the values of 0.19−0.23 $mol{\cdot}L^{-1}{\cdot}bar^{-1}$ in CCl_4 at −10 to 0 °C.[58] In liquid CO_2 at ∼7 °C and 6.9 MPa, ozone has been reported to oxidize dilute cyclohexane (∼0.6 mol/L CO_2) to predominantly cyclohexanone at yields up to 18%.[29] However, only 12−21% of the oxidizing equivalents from ozone were utilized for producing oxygenates. Given the relatively high cost of ozone, high oxidant utilization is required for a sustainable process.

Recently, we showed that ozone concentration can also be pressure-tuned in condensed isobutane at ambient temperatures (16−18 °C) but much milder pressures (up to 0.7 MPa).[30] This process avoids the use of any additional solvent. Like liquid CO_2, liquefied light alkanes (C_2−C_4) exhibit properties tunable with pressure. While these alkanes exist as gases at ambient conditions, they condense at relatively mild pressures because their critical temperatures are fairly close to ambient. They dissolve ozone potentially as well as CO_2 and CCl_4.[58] In condensed isobutane, highly selective ozonation was observed to produce *tert*-butyl alcohol (TBA) as the main product. Because the reaction was performed in the condensed isobutane phase, we could take advantage of liquid additives to control reactivity. For example, we observed that protic additives such as water significantly improve ozone utilization for TBA formation. Further, by controlling the oxidant partial pressure, the gas phase above the condensed hydrocarbon phases can be easily maintained outside the flammability region, and the oxidant concentrations in the liquid phase can be tuned to avoid over-oxidation. It must be noted that isobutane ozonation in the gas phase, which exists in equilibrium with the condensed phase, is kinetically limited. Thus, ozonation occurs predominantly in the liquid phase. These observations suggested that similar pressure-tuning of condensed phase ozonation might be harnessed for achieving ozonation of the more challenging linear alkanes with high carbon atom economy.

In this work, we investigated the ozonation of linear light alkanes, propane, and *n*-butane, either alone or each in a mixture with isobutane, at ambient temperature and mild pressures to generate a condensed alkane phase. In such media, the unique tunability of ozone concentration is harnessed for facile activation of the alkanes and to avoid over-oxidation of the products. To the best of our knowledge, our work is the first to report such alkane ozonation, along with a relatively comprehensive analysis of possible products by GC/FID, GC/TCD, and NMR. We demonstrate the ability to control product selectivity and ozone utilization by adding protic additives and/or isobutane in the feed. Such tunability and the incorporation of liquid additives to direct selectivity, keys to achieving high carbon atom economy toward oxygenated products, cannot be achieved in gas-phase ozonations. The strategies demonstrated herein drastically enhance the utilization of ozone toward the activation of secondary C−H bonds than previously reported. The formation of alcohols with high C atom and ozone economy at mild conditions offers an alternate route for olefin formation via alcohol dehydration. Such a route demands less energy than the endothermic dehydrogenation of alkanes, followed by distillation to separate the paraffin+olefin mixture. While the cost of ozone may challenge the economic viability of the ozonation route, recent advances in electrochemical ozone production[59] could alleviate this problem.

■ METHODS

Materials

The dioxygen (UHP Plus), argon (HP), propane (UHP), *n*-butane (UHP), and isobutane (UHP) were all purchased from Matheson.

Experimental Methods

The apparatus and procedure of the experiments have been described in detail in an earlier publication,[30] with some modifications to the reaction procedure for propane, as well as the analysis procedure by gas chromatography (SI Section 1.2) for the complex liquid product mixture. Briefly, a Parr reactor is used with a Teflon insert in the reactor along with a shaft and a thermowell coated with Teflon to prevent ozone decomposition on the metal surfaces.

A dioxygen stream is used to generate a mixture of ozone and dioxygen with the desired ozone mole fraction by an Atlas ozone generator and charged into a reservoir equipped with a pressure transducer.[57] Ar is then added into the reservoir to a desired pressure. Unless otherwise mentioned, the mixture contains about 5% O_3 and 45% O_2, with the balance being Ar. A Teflon-lined Parr vessel is evacuated at 80 °C under vacuum. The reactor is cooled and charged with the desired amounts of liquid alkanes (0.3 mol total alkanes) from an ISCO syringe pump cooled to 10 °C. An option to direct the liquid alkane stream through a sample loop containing distilled water is provided to meter in controlled amounts of water. The reactor stirrer is set at 1000 rpm to allow the reactor to stabilize at the laboratory temperature of around 24−25 °C. Throughout a semi-batch run, the $O_2 + O_3 + Ar$ mixture is supplied continuously to the reactor via a pressure regulator maintained at a constant pressure. The reaction conditions are provided in figure captions. The alkanes that escape with the gas phase are partially condensed in a cold trap held around −60 to −50 °C and ambient pressure to concentrate the CO_2.

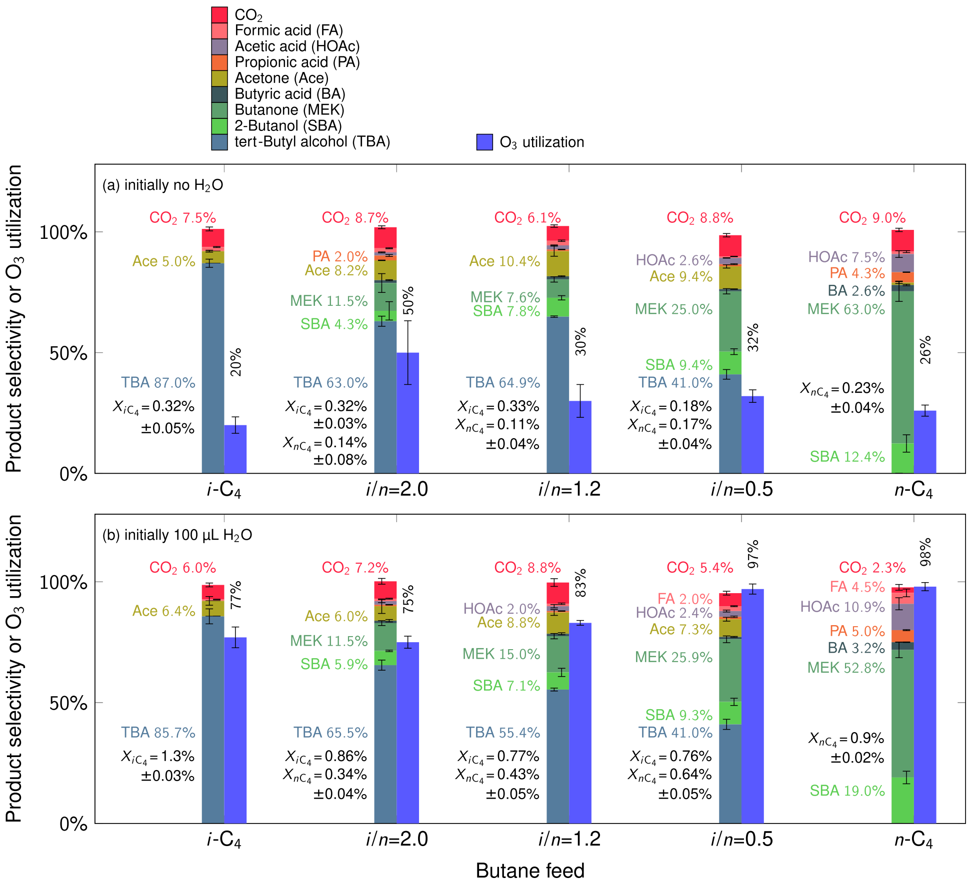


Figure 1. Tuning product distribution and ozone utilization by isobutane and water addition during the ozonation of various *n*-butane + isobutane mixtures. *Reaction conditions*: 25 °C, 3.1 ± 0.1 mmol of O_3, 0.34 MPa $O_3 + O_2$ + Ar partial pressure, average residence time ∼6 min. *Note*: "*i*-C_4" represents isobutane, "*n*-C_4" represents *n*-butane, and "$i/n = x$" represents a mixture with isobutane/*n*-butane molar ratio of *x*.

The gas from the condenser is collected in Tedlar sample bags. At the end of a run, the reactor is placed in an ice bath kept in a freezer at −18 °C. At this temperature, the vapor pressures of all compounds remaining in the reactor are very low (SI Section 1.1). Then, a weighed amount of cold methanol is added into the reactor, and the reactor is kept at around 0−4 °C to allow the remaining alkanes to vaporize and be condensed in the cold trap. The trap is maintained at around −60 to −50 °C for butanes, and around −90 °C when propane is present. After adding 2-pentanone as an internal standard, the methanolic liquid sample is injected into an Agilent 7890A GC equipped with a flame ionization detector (FID) and a HP-PLOT/Q column to resolve ≥C_2 products. The methanolic liquid sample is also added to D_2O with maleic acid as an internal standard to quantify formic acid by ^1H NMR spectroscopy. The gas samples collected in Tedlar bags were injected into another GC equipped with a thermal conductivity detector to analyze the CO_2 and an FID to analyze the hydrocarbons. More details of the GC/FID analytical methods, including a sample chromatogram, are provided in SI Section 1.3.

The details of estimating alkane conversion (*X*), molar product selectivity, and O_3 utilization (*U*), as well as their confidence intervals, are provided in SI Section 1.4. The O_3 utilization is characterized by the ratio of utilized oxidizing equivalents from ozone/theoretical maximum oxidizing equivalents.

■ RESULTS AND DISCUSSION

Ozonation of *n*-Butane

Although light alkane ozonation shares some common initiation mechanisms,[60] *n*-butane as a sole substrate yields a more complex product spectrum (rightmost group in Figure 1) compared to isobutane as a sole substrate (leftmost group in Figure 1). The major products from *n*-butane ozonation include 2-butanol, butanone, monocarboxylic acids, and CO_2. Sequential formation of 2-butanol, 2-butanone, and eventually carboxylic acids is possible. Rakovsky et al. have reported that in CCl_4, the ozonation of dilute 2-butanol yields butanone via an intermediate with geminal hydroxyl and hydrotrioxyl groups,[49] and ozone reacts further with the ketone to produce acetic acid, 2,3-butanedione (diacetal), and a hydroperoxide.[48] In separate experiments at ambient pressure and −20 to −10 °C, we confirmed that at the ozone/dioxygen fractions used in our work, either a neat substrate (2-butanol or butanone) or a mixture of these substrates in CCl_4 can be oxidized; 2-butanol to butanone; and butanone to acids, 3-hydroxybutanone, and 2,3-butanedione. Given that high concentrations of both *tert*-butyl hydroperoxide and ozone mutually promote their decomposition possibly by forming excess free radicals,[30,61−64] we infer that hydroperoxide may not form in significant amounts at the conditions used in our work where high ozone utilization is observed. As for 3-hydroxybutanone and 2,3-butanedione as oxidation products from butanone, they form in significant amounts only at relatively high concentrations of either 2-butanol or butanone.

Other possible routes for butanone formation include the direct elimination of a HOOH[29] or a HOOOH[65] from the respective polyoxide $(CH_3CH_2)(CH_3)HC{-}O_nH$ ($n = 2$ or 3). Traces of proton signals from −OOH groups are reported in the product mixtures in the previous work[30] and also observed in this work. However, the origin of the hydroperoxide is unclear, since the ozonation of ketones and alcohols also produces hydroperoxide.[48] Thus, the proton signals alone are insufficient to support the hydrogen peroxide elimination pathway. The observed overall stoichiometry of more than one mole oxygenate formation per mole of ozone consumption could be related to oxidation by polyoxides (trioxide or peroxide). The high ozone utilization generally observed in our work suggests that peroxide could not exist in high concentrations. Further, peroxides cannot possibly activate butanols[66−68] and butanes without a catalyst at ambient temperature. Therefore, trioxides are more likely involved, although, at ambient temperature, they are probably too unstable[62,65] to observe by ^{1}H NMR spectroscopy.[69]

Due to the reactivity gap between *n*-butane and the products, including 2-butanol and butanone, the foregoing over-oxidation is likely more competitive at consuming ozone compared to the alkane activation. Nonetheless, our biphasic gas−liquid process for *n*-butane ozonation results in low CO_2 formation (9%), especially compared to gas-phase ozonation (up to 78%), and has the added advantage of not employing any halogenated solvent (*e.g.*, CCl_4). Because isobutane has been demonstrated to be more reactive than *tert*-butyl alcohol (TBA) during ozonation at similar conditions,[30] we next explored the use of isobutane to suppress product over-oxidation.

Ozonation of Mixtures of *n*-Butane and Isobutane

In addition to evaluating the tunable selectivity in condensed phases, assessing the ozonation of butane mixtures may provide an alternate route for processing natural gas liquids without fractionation. While the C_3 and C_4 fractions in natural gas liquids exhibit a relatively wide volatility gap, such is not the case between *n*-butane and isobutane within the C_4 fraction (SI Section 1.1a). In other words, separation of the C_4 alkanes is more challenging and energy-intensive by the distillation route.[70] Hence, butane mixtures with different compositions were investigated with ozone at (25.0 ± 0.6) °C to evaluate the effect of initial composition of the butane mixture on the observed products. Specifically, an isobutane to *n*-butane ratio (*i*/*n*) of 1.2 simulates the published butane composition in a natural gas sample,[71] while the other *i*/*n* ratios serve as a sensitivity test due to the naturally varying compositions. The experiments were performed with either 100 μL (5.53 mmol) water addition or no initial water addition. It must be noted that water is a byproduct of the reactions forming C=O bonds. In the case of *n*-butane + isobutane mixtures, water formation as byproduct ranges from 0.1−0.2 and 0.5−0.8 mmol without and with initial water addition, respectively. With only *n*-butane as feed, 0.5 and 2.2 mmol water form without and with initially added water, respectively. Such amounts are smaller compared to the added water (5.53 mmol) essential for effective ozone utilization.

The major products (defined as those having measured selectivity >0.1%) from neat isobutane ozonation include *tert*-butyl alcohol (TBA), acetone, formic acid, and CO_2, along with the negligible formation of isobutyl alcohol, isobutyraldehyde, and *tert*-butyl hydroperoxide. As shown in Figure 1, *n*-butane alone as feed produces a complex oxygenate mixture, including 2-butanol, butanone, butyric acid, propionic acid, acetic acid, and formic acid, accompanied by CO_2. Small quantities of hydroperoxide (most likely 2-hydroperoxybutane) and acetone also form. Despite the low yields, the peroxides could be a potential hazard during further processing if not decomposed.[72]

The introduction of isobutane to the feed produced an unanticipated significant effect on product distribution. Along with butane conversions and ozone utilization, Figure 1 shows detailed product distributions, while Figure 2 summarizes the effect of isobutane and water addition on *n*-butane conversion and product selectivity. The *n*-butane conversion and ozone utilization increase three to fourfold with initial water addition (Figure 1b) than without it (Figure 1a). Either with or without water addition, both ozone utilization and ketones selectivity increase with increasing *n*-butane fraction in the feed. These results suggest that 2-butanol is highly reactive with ozone, with the oxidation to butanone consuming more ozone than the oxidation to 2-butanol. In contrast, *tert*-butyl alcohol is significantly more stable in the presence of ozone (ratio of overall oxidation rate for TBA/2-butanol ≈ 10^{-2}),[49] even at relatively high ozone content, as previously demonstrated.[30] In sharp contrast, ketone and acid formation from *n*-butane is less when isobutane is added to the feed up to an *i*/*n* = 2 (Figure 2), suggesting the C=O formation and C−C cleavage reactions are suppressed by the addition of isobutane. The progressive increase in isobutane content in the mixed C_4 feed tunes the product distribution (Figure S3). The butanone/2-butanol ratio decreases with isobutane addition (2.8 for neat *n*-butane and 1.9 for *i*/*n*=2.0), indicating that isobutane intercepts ozone to preferentially form TBA, thereby preventing further oxidation of the alcohol to ketone. This trend also suggests that 2-butanol oxidation is likely a significant route for butanone formation.

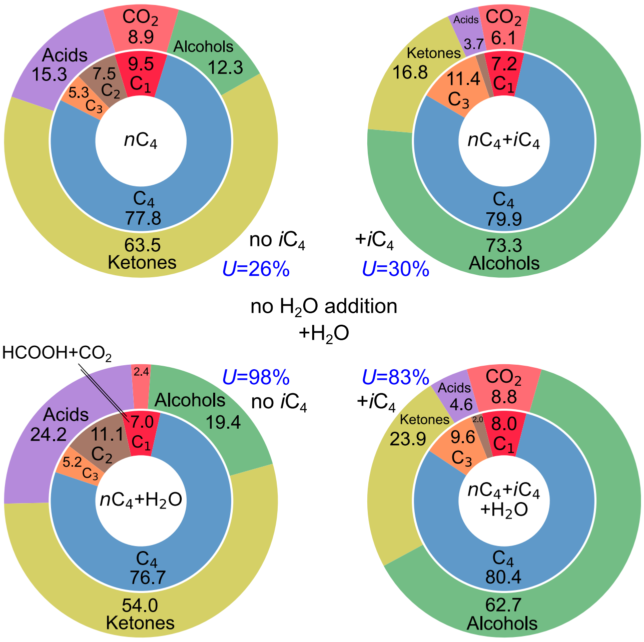


Figure 2. Tuning product distribution by isobutane and water addition during the ozonation of various *n*-butane + isobutane mixtures. *Reaction conditions*: 25 °C, 3.1 ± 0.1 mmol of O_3, 0.34 MPa O_3 + O_2 + Ar partial pressure, average residence time ~6 min.

Mixtures of Isobutane and Propane

Motivated by the beneficial effect of isobutane presence in mixed butane feed, mixtures of isobutane and propane were also evaluated. Unlike butane mixtures, the vapor pressures of propane + isobutane mixtures vary substantially in the range of the feed compositions studied, from 0.56 to 0.98 MPa. The reactor was pressurized with O_3 + O_2 + Ar mixtures such that both the O_3 and O_2 partial pressures were nearly invariant in all cases.

Based on the products from *n*-butane ozonation, propane ozonation is expected to produce isopropyl alcohol (IPA), acetone, acetic acid, formic acid, and CO_2. However, acetic acid was not observed in any run (selectivity ≪ 0.03%). Such observation suggests that the C_3 oxygenates are more prone to complete cleavage to C_1 products compared to the C−C cleavage of butanone. The absence of acetic acid also suggests that the enol tautomer−ozone route[48,73] is probably less significant for acetone. As shown in Figure 3, with only propane in the feed, the CO_2 selectivity is ~66%. Similarly, high CO_2 selectivity was also reported in gas-phase ozonation of propane at 50 °C.[27,28] The C_3 oxygenates are likely much more reactive with ozone compared to propane.[74,75] As such, the effect of isobutane addition is even more pronounced for propane compared to *n*-butane. Adding 33 mole % isobutane doubles the IPA yield compared to neat propane and diminishes the CO_2 selectivity drastically to ~16% while increasing the overall hydrocarbon conversion. At 66 mole % isobutane in the feed, the CO_2 selectivity drops even further to ~9% (Figure S4). Although the net oxidizing equivalents from ozone are similar in each case, ozone utilization is drastically shifted toward the desired oxygenate formation. The increased formation of IPA in the presence of isobutane at mild conditions is remarkable and suggests a potential low-energy route for making propene from propane via IPA dehydration. Since acetone forms from both propane and isobutane ozonation, it is difficult to quantify the acetone produced from propane. However, an estimate could be made assuming that formic acid and CO_2 are (a) byproducts of acetone formation from isobutane and (b) products of complete C−C cleavage from propane ozonation (Scheme S1). For isobutane/propane ratios of 1−2, based on the ratios of (formic acid + CO_2)/acetone (SI Section 1.4), it is estimated that at most two-thirds of the acetone forms from isobutane, *i.e.*, at least one-third of the acetone forms from propane.

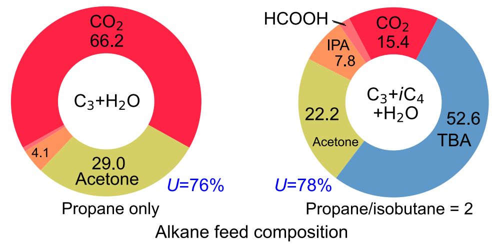


Figure 3. Tuning product distribution and ozone utilization by isobutane during the ozonation of various propane + isobutane mixtures with initially added water. *Reaction conditions*: 24 °C, 5.53 mmol of water, 2.6 ± 0.1 mmol of O_3, 0.24 MPa O_3 + O_2 + Ar partial pressure, average residence time ~ 15 min.

Interestingly, only for neat propane, the product distribution from the three runs varied more than the other cases. Whiting et al. reported that the product distribution from IPA ozonation depends on the alcohol source,[73] suggesting that feed impurities may affect radical formation and, thereby, the reaction pathways. The large deviations in product selectivities between repeated runs along with the high CO_2 formation (Figure S4) suggest free radicals-facilitated oxidation route that is potentially sensitive to impurities during propane ozonation. The isobutane addition to propane appears to inhibit such an unstable route by utilizing the ozone toward TBA formation, allowing much better control on the selectivity toward the desired products.

Ozonation of a Mixture of Butanes and Propane

Isobutane has been shown to suppress over-oxidation when added to *n*-butane and propane, possibly by competing against the products (secondary alcohols and ketones) for ozonation. However, the actual C_3 and C_4 compositions in natural gas liquids vary significantly due to the geological conditions.[6,71,76] The propane/isobutane ratio could be much higher (*e.g.*, ~11)[76] than those in the foregoing experiments. As such, a slower overall activation rate might be expected during ozonation of C_3 and C_4 fractions, which could be detrimental to ozone utilization. By adding water and tuning ozone concentration in the liquid phase (by adjusting the partial pressure in the gas phase), improved ozone utilization could be achieved, as demonstrated by the preliminary results in Figures 4 and 5. The ternary feed used in these experiments simulates the propane, *n*-butane, and isobutane fractions found in typical natural gas samples.[76,77] In sharp contrast to the progressive increase in ozone utilization when adding water (up to 27.7 mmol water) to the isobutane feed,[71] the ozone utilization

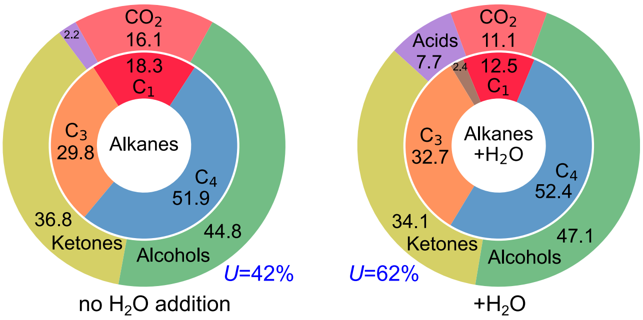


Figure 4. Tuning product distribution and ozone utilization by the quantity of initially added water during the ozonation of a propane + *n*-butane + isobutane mixtures. *Reaction conditions*: Propane/*n*-butane/isobutane = 32:9:9, 24 °C, 2.0 ± 0.1 mmol of O_3, 0.24 MPa O_3 + O_2 + Ar partial pressure, average residence time ~ 15 min.

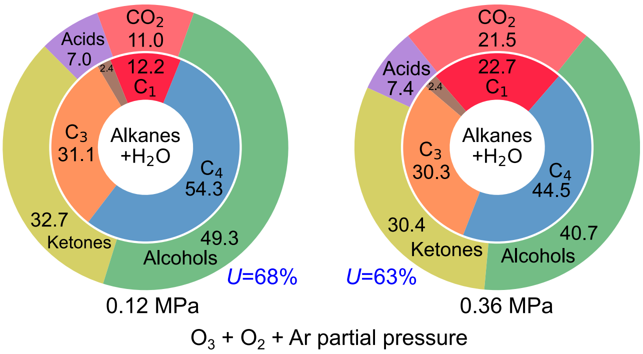
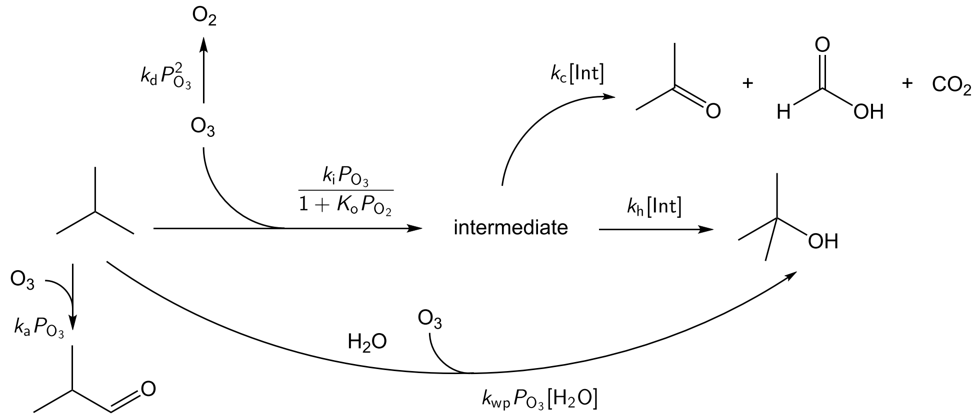


Figure 5. Tuning product distribution and ozone utilization by the partial pressure of the O_3 + O_2 + Ar mixture during the ozonation of a propane + *n*-butane + isobutane mixtures. *Reaction conditions*: Propane/*n*-butane/isobutane = 32:9:9, 24 °C, 5.53 mmol of H_2O, 2.0 ± 0.1 mmol of O_3, average residence time ~ 15 min.

https://doi.org/10.1021/jacsau.2c00631
JACS Au 2023, 3, 498−507

Scheme 1. Possible Reaction Routes Inferred from the Mass Balance Equations



changes only marginally beyond 5.53 mmol water addition to the C_3 + C_4 mixture (Figure S5). Meanwhile, excess water promotes over-oxidation, forming acids and CO_2. As shown in Figure S6, a relatively low ozone partial pressure of 6 kPa (=5% × 0.12 MPa) is most beneficial for minimizing ozone decomposition and product over-oxidation. As inferred from Figure S6, the decrease in ozone utilization is milder at lower ozone partial pressures (between 12 and 18 kPa) compared to that observed during isobutane ozonation (between 17 and 24 kPa).[71]

In contrast to isobutane ozonation, where the relatively stable TBA is produced,[71] greater product over-oxidation is observed in the case of mixed alkane feed. This is expected as the more reactive products, the secondary alcohols and ketones, may be oxidized more readily than the linear alkanes. In theory, this should have promoted ozone utilization. However, the opposite trends of ozone utilization with ozone partial pressure in Figure S6 suggest that the ozone solubility may be different in propane and isobutane, resulting in differences in ozone decomposition kinetics. Various mechanisms of ozone decomposition[78,79] may coexist, characterized by either a first-order or a second-order decomposition kinetics in the gas phase.[80] Such mixed reaction orders likely occur in the liquid phase as well. The relatively minor changes in product distribution and ozone utilization at low ozone partial pressures in Figure S6 suggest that the apparent reaction orders for ozone decomposition and alkane activation are similar with respect to ozone (likely around first order). As ozone concentration increases, its decomposition may shift to higher apparent order in the liquid phase. This hypothesis was tested in the kinetic model discussed in the next section, which confirms that ozone decomposition and alkane activation can indeed exhibit different reaction orders in liquid isobutane, thereby explaining the more varied effects of ozone partial pressure on ozone utilization.[71]

Empirical Kinetic Modeling of Isobutane Ozonation

All ozonation experiments in this work were carried out in a large excess of the alkane(s) in the liquid phase with good mixing that eliminates gas−liquid mass transfer limitations (SI Section 3.2). The ozone and dioxygen concentrations in the liquid phase are dictated by their partial pressures in the gas phase. The substrate conversion in these experiments is very low (<2%), making the data ideal for kinetic modeling and analysis. However, the large number of ozonation products from mixed alkanes renders any modeling effort rather challenging. Given that isobutane forms fewer products and its presence has a major influence on product selectivities during the ozonation of mixed alkanes, we decided to model the kinetics of neat isobutane ozonation. In the previous work,[30] we reviewed the possible routes and mechanisms for isobutane ozonation from the literature. Following the observations therein, we designed experiments to establish a relatively simple empirical model for isobutane ozonation that provides further clues about the possible reaction routes. The experimental details, the raw data, the various kinetic models tested, and the model regression procedure are detailed in SI Section 3. The rival kinetic models were assessed based on the relative quality of model predictions of the experimental data. Based on this procedure, the reaction network that best describes the experimental data on isobutane ozonation (see Figure S7) is as shown in Scheme 1. Table 1 shows values of the various kinetic parameters regressed from the experimentally observed product yields.

Table 1. Empirical Kinetic Parameters for Isobutane Ozonation

constant	value
k_d	$(8.33 \pm 0.03) \times 10^{-1}$ mol·(L·min·bar^2)$^{-1}$
K_o	$(6.98 \pm 0.02) \times 10^{-1}$ bar^{-1}
k_i	$(3.56 \pm 0.02) \times 10^{-2}$ mol·(L·min·bar)$^{-1}$
k_c	$(1.20 \pm 0.02) \times 10^{-1}$ min^{-1}
k_h	(1.00 ± 0.02) min^{-1}
k_{wp}	$(3.87 \pm 0.09) \times 10^{-4}$ min^{-1}·bar^{-1}
k_a	$(7.38 \pm 6.51) \times 10^{-5}$ mol·(L·min·bar)$^{-1}$
k_f	$(6.65 \pm 1.80) \times 10^{-2}$

At the low substrate conversions, the isobutane concentration is assumed to be invariant (≈the density of pure isobutane 9.47 mol/L) in the experiments and thus absorbed into the rate constants k_i, k_a, and k_{wp}. The first-order dependence of isobutane activation rate on ozone partial pressure (P_{O_3}) is consistent with previously reported mechanisms.[30,65,81,82]

Compared to the estimated ranges of rate constants for propane and isobutane dehydrogenation on a variety of heterogeneous catalysts [~0.3 to 6 mol$_{alkane}$/(L·min), assuming a catalyst packing density ~ 1 kg/L] at temperatures >450 °C,[17,83] the estimated rate constant for isobutane activation by ozone (k_i) is of a similar magnitude. This suggests that isobutane activation in its condensed phase by ozone is as facile at ambient temperature as its catalytic conversion by dehydrogenation at much higher temperatures.

The model additionally reveals a second-order dependence of the ozone decomposition rate on P_{O_3}. Compared to the typical rates of O_3 decomposition in the gas phase,[78,80] the O_3 decomposition here occurs predominantly in the liquid phase. In addition, an apparent inhibition by dioxygen is revealed [as seen in the denominator of the $k_iP_{O_3}/(1 + K_oP_{O_2})$ term], especially at low P_{O_3}. The initiation steps of saturated hydrocarbons with ozone have been proposed to involve radical formation as follows.[48,60]

$$\mathrm{R{-}H + O_3 \rightarrow R^\bullet + HOOO^\bullet \rightarrow ROOOH}$$
$$\mathrm{\rightarrow RO^\bullet + HOO^\bullet}$$

$$\mathrm{RO^\bullet + R{-}H \rightarrow ROH + R^\bullet}$$

$$\mathrm{R^\bullet + O_3 \rightarrow ROOR^\bullet}$$

The $R^\bullet$ radical may be intercepted by dioxygen to produce a less active peroxyl intermediate, slowing down the overall activation rate.[48,84]

$$\mathrm{R^\bullet + O_2 \rightarrow ROO^\bullet}$$

Thus, this inhibition effect could be evidence that the assumed intermediate shared by acetone and *tert*-butyl alcohol formation is likely to be *tert*-butyl hydrotrioxide or its derivative. As suggested by the observations during the ozonation of butanone[48] and isobutane, dioxygen potentially inhibits other reactions involving H-atom abstraction during the initiation steps, such as the ozonation of 2-butanol[48,85] and *n*-butane.

Interestingly, the term expressing the water effect, $k_{wp}P_{O_3}[H_2O]$, describes a first-order dependence each on the water concentration and the ozone partial pressure but not on the concentration of the assumed intermediate shared by acetone and TBA formation (eq S4 and Figure S8c). Thus, water appears to promote a different route to form TBA from isobutane, most likely involving multiple elementary reactions. Similar to the reported mechanisms during water treatment, ozone and water may also produce a pool of various species, including H_2O_x (neutral, x = 2 or 3) and HO_y (radical or anionic, y = 1−5), which may interconvert[86−90] and promote the activation of organic molecules.[91] The water effect in this model may be a lumped representation of the formation of one or multiple intermediates from ozone and water, which then favor hydrogen abstraction from isobutane molecules. Further experimental mechanistic investigations, complemented by theory, are needed to gain better fundamental insights.

The foregoing results of mixed alkane ozonation demonstrate that increasing isobutane content in the mixed alkane feed dictates product selectivity by (a) tuning the ozone availability in the liquid phase and (b) preferentially utilizing ozone to form active intermediates that not only promote the formation of tertiary butyl alcohol but also convert the linear alkanes in the feed to liquid oxygenates, while minimizing CO_2 formation. The product yields may be further optimized by fine-tuning the reaction conditions (isobutane content in feed, O_2 and O_3 partial pressures, and protic additives, in particular) to maximize ozone utilization and the yield of valuable liquid oxygenates. Detailed studies of the solubility and decomposition of ozone in various liquid alkane media are needed to provide more insights into such optimization.

■ CONCLUSIONS

We have demonstrated the oxidation of mixed light alkanes by ozone to liquid oxygenates with high carbon atom economy (>90% combined selectivity to oxygenates and CO_2 < 10%) in their condensed phases at ambient temperature and mild pressures. This is a significant improvement over the 55−78% CO_2 selectivities reported for the gas-phase ozonation at 50 °C. The novelty demonstrated in our work is twofold. First, we are able to control the ozone solubility, and therefore its availability, in the liquid phase by simply tuning the gas-phase partial pressure. The significantly higher substrate concentrations in liquid phase compared to gas-phase ozonation likely promote alkane activation even at ambient temperature. Thus, the biphasic nature of the reaction processes promotes effective utilization of ozone to create valuable alkane oxygenates rather than CO_2. Second, the addition of protic solvents to the liquid phase can direct preferred reaction pathways, which is challenging in a low-density gas phase. When water is added to the feed mixture, ozone utilization increases with concurrent increases in alkane conversions and selectivity toward oxygenated products, with even less CO_2 formation. The beneficial effects of adding isobutane and water are especially pronounced with a mixed feed of propane and isobutane. These additives, along with the facile tunability of ozone concentrations in light hydrocarbon liquid phases, can be harnessed to maximize ozone utilization and C atom economy, promoting decarbonization and sustainability. This demonstration of facile and safe production of oxygenates, including alcohols, by a direct route from alkanes with high carbon atom economy and ozone utilization should elevate the promise of natural gas liquids as a viable feedstock for the chemical industry. The results presented herein suggest potential application in selective hydroxylation of C−H bonds in other substrates such as those encountered in pharmaceutical processing and certain polymers. The concept can also be potentially used in the chemical upcycling of polyolefin plastic wastes wherein the C−H bonds are functionalized and/or severed to yield smaller molecules of value.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.2c00631.

Reaction and analysis procedures modified from previous work, and details of the empirical model for isobutane ozonation (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Bala Subramaniam − *Center for Environmentally Beneficial Catalysis, University of Kansas, Lawrence, Kansas 66047, United States; Department of Chemical and Petroleum Engineering, University of Kansas, Lawrence, Kansas 66045, United States;* orcid.org/0000-0001-5361-1954; Email: bsubramaniam@ku.edu

Authors

Hongda Zhu − *Center for Environmentally Beneficial Catalysis, University of Kansas, Lawrence, Kansas 66047, United States*

Timothy A. Jackson − *Center for Environmentally Beneficial Catalysis, University of Kansas, Lawrence, Kansas 66047, United States; Department of Chemistry, University of Kansas, Lawrence, Kansas 66045, United States;* orcid.org/0000-0002-3529-2715

Complete contact information is available at: https://pubs.acs.org/10.1021/jacsau.2c00631

Author Contributions

CRediT: **Hongda Zhu** conceptualization, data curation, formal analysis, investigation, methodology, writing-original draft; **Timothy A. Jackson** formal analysis, methodology, supervision, validation, writing-review & editing; **Bala Subramaniam** conceptualization, formal analysis, funding acquisition, project administration, resources, supervision, validation, writing-review & editing.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are grateful for the support from the National Science Foundation Award Number 2119754. The authors also acknowledge the support for the NMR spectrometer by the National Institute of Health Shared Instrumentation Grant Number S10OD016360.

■ REFERENCES

(1) Amghizar, I.; Vandewalle, L. A.; Van Geem, K. M.; Marin, G. B. New Trends in Olefin Production. *Engineering* **2017**, *3*, 171−178.

(2) Galadima, A.; Muraza, O. Revisiting the Oxidative Coupling of Methane to Ethylene in the Golden Period of Shale Gas: A Review. *J. Ind. Eng. Chem.* **2016**, *37*, 1−13.

(3) Galadima, A.; Muraza, O. Advances in Catalyst Design for the Conversion of Methane to Aromatics: A Critical Review. *Catal. Surv. Asia* **2019**, *23*, 149−170.

(4) Wood, D. A.; Nwaoha, C.; Towler, B. F. Gas-to-liquids (GTL): A Review of an Industry Offering Several Routes for Monetizing Natural Gas. *J. Nat. Gas Sci. Eng.* **2012**, *9*, 196−208.

(5) Fei, Q.; Guarnieri, M. T.; Tao, L.; Laurens, L. M. L.; Dowe, N.; Pienkos, P. T. Bioconversion of Natural Gas to Liquid Fuel: Opportunities and Challenges. *Biotechnol. Adv.* **2014**, *32*, 596−614.

(6) Ridha, T.; Li, Y.; Gençer, E.; Siirola, J. J.; Miller, J. T.; Ribeiro, F. H.; Agrawal, R. Valorization of Shale Gas Condensate to Liquid Hydrocarbons through Catalytic Dehydrogenation and Oligomerization. *Processes* **2018**, *6*, 139−159.

(7) Chen, Q.; Dunn, J. B.; Allen, D. T. Greenhouse Gas Emissions of Transportation Fuels from Shale Gas-Derived Natural Gas Liquids. *Procedia CIRP* **2019**, *80*, 346−351.

(8) Ganesh, H. S.; Dean, D. P.; Vernuccio, S.; Edgar, T. F.; Baldea, M.; Broadbelt, L. J.; Stadtherr, M. A.; Allen, D. T. Product Value Modeling for a Natural Gas Liquid to Liquid Transportation Fuel Process. *Ind. Eng. Chem. Res.* **2020**, *59*, 3109−3119.

(9) Honkela, M. L.; Ouni, T.; Krause, A. O. I. Thermodynamics and Kinetics of the Dehydration of tert-Butyl Alcohol. *Ind. Eng. Chem. Res.* **2004**, *43*, 4060−4065.

(10) Roy, S.; Mpourmpakis, G.; Hong, D.-Y.; Vlachos, D. G.; Bhan, A.; Gorte, R. J. Mechanistic Study of Alcohol Dehydration on γ-Al_2O_3. *ACS Catal.* **2012**, *2*, 1846−1853.

(11) Knözinger, H.; Scheglila, A. The Dehydration of Alcohols on Alumina: XII. Kinetic Isotope Effects in the Olefin Formation from Butanols. *J. Catal.* **1970**, *17*, 252−263.

(12) Cavani, F.; Ballarini, N.; Cericola, A. Oxidative Dehydrogenation of Ethane and Propane: How Far from Commercial Implementation? *Catal. Today* **2007**, *127*, 113−131.

(13) Hermans, I.; Grant, J. T.; Carrero Marquez, C.; Chieregato, A.; Venegas, J. M. Heterogeneous Catalysts for the Oxidative Dehydrogenation of Alkanes or Oxidative Coupling of Methane. US109611702021.

(14) Sattler, J. J. H. B.; Ruiz-Martinez, J.; Santillan-Jimenez, E.; Weckhuysen, B. M. Catalytic Dehydrogenation of Light Alkanes on Metals and Metal Oxides. *Chem. Rev.* **2014**, *114*, 10613−10653.

(15) Hermans, I. Overview of Radical Chain Oxidation Chemistry. In *Liquid Phase Aerobic Oxidation Catalysis: Industrial Applications and Academic Perspectives*, Wiley, 2016; pp 1−14.

(16) Hermans, I.; Spier, E. S.; Neuenschwander, U.; Turrà, N.; Baiker, A. Selective Oxidation Catalysis: Opportunities and Challenges. *Topics Catal.* **2009**, *52*, 1162−1174.

(17) Venegas, J. M.; McDermott, W. P.; Hermans, I. Serendipity in Catalysis Research: Boron-Based Materials for Alkane Oxidative Dehydrogenation. *Acc. Chem. Res.* **2018**, *51*, 2556−2564.

(18) Fang, G.; Lin, J.; Wang, X. Low-temperature Conversion of Methane to Oxygenates by Supported Metal Catalysts: From Nanoparticles to Single Atoms. *Chin. J. Chem. Eng.* **2021**, *38*, 18−29.

(19) Coperet, C. C−H Bond Activation and Organometallic Intermediates on Isolated Metal Centers on Oxide Surfaces. *Chem. Rev.* **2010**, *110*, 656−680.

(20) Dalton, T.; Faber, T.; Glorius, F. C−H Activation: Toward Sustainability and Applications. *ACS Cent. Sci.* **2021**, *7*, 245−261.

(21) Wencel-Delord, J.; Dröge, T.; Liu, F.; Glorius, F. Towards Mild Metal-Catalyzed C−H Bond Activation. *Chem. Soc. Rev.* **2011**, *40*, 4740−4761.

(22) Shilov, A. E.; Shul'pin, G. B. Activation of C−H Bonds by Metal Complexes. *Chem. Rev.* **1997**, *97*, 2879−2932.

(23) Sauermann, N.; Meyer, T. H.; Qiu, Y.; Ackermann, L. Electrocatalytic C−H Activation. *ACS Catal.* **2018**, *8*, 7086−7103.

(24) Najari, S.; Saeidi, S.; Concepcion, P.; Dionysiou, D. D.; Bhargava, S. K.; Lee, A. F.; Wilson, K. Oxidative Dehydrogenation of Ethane: Catalytic and Mechanistic Aspects and Future Trends. *Chem. Soc. Rev.* **2021**, *50*, 4564−4605.

(25) Linstrom, P. J.; Mallard, W. G., *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*.

(26) Suresh, A. K.; Sharma, M. M.; Sridhar, T. Engineering Aspects of Industrial Liquid-Phase Air Oxidation of Hydrocarbons. *Ind. Eng. Chem. Res.* **2000**, *39*, 3958−3997.

(27) Schubert, C. C.; Schubert, S. J.; Pease, R. N. The Oxidation of Lower Paraffin Hydrocarbons. I. Room Temperature Reaction of Methane, Propane, *n*-Butane and Isobutane with Ozonized Oxygen. *J. Am. Chem. Soc.* **1956**, *78*, 2044−2048.

(28) Morrissey, R. J.; Schubert, C. C. S. J. The Reactions of Ozone with Propane and Ethane. *Combust. Flame* **1963**, *7*, 263−268.

(29) Chen, X.; Rice, D. B.; Danby, A. M.; Lundin, M. D.; Jackson, T. A.; Subramaniam, B. Experimental and Computational Investigations of C−H Activation of Cyclohexane by Ozone in Liquid CO_2. *React. Chem. Eng.* **2020**, *5*, 793−802.

(30) Zhu, H.; Jackson, T. A.; Subramaniam, B. Highly Selective Isobutane Hydroxylation by Ozone in a Pressure-Tuned Biphasic Gas−Liquid Process. *ACS Sustainable Chem. Eng.* **2021**, *9*, 5506−5512.

(31) Pullabhotla, V. S. R. R.; Jonnalagadda, S. B. Scope of Metal Loaded Microporous Zeolite-Y as Catalyst in Ozone Initiated Oxidation of *n*-hexadecane. *J. Adv. Oxid. Technol.* **2009**, *12*, 178−187.

(32) Rajasekhar Pullabhotla, V. S. R.; Southway, C.; Jonnalagadda, S. B. Ozone Initiated Oxidation of Hexadecane with Metal Loaded γ-Al_2O_3 Catalysts. *Catal. Lett.* **2008**, *124*, 118−126.

(33) Pullabhotla, V. S. R. R.; Jonnalagadda, S. B. Oxidation of Higher Alkanes at Moderate Reaction Conditions with Ozone in

Presence of Mesoporous Materials. *J. Adv. Oxid. Technol.* **2008**, *11*, 445−454.

(34) Dhandapani, B.; Oyama, S. T. Gas Phase Ozone Decomposition Catalysts. *Appl. Catal., B* **1997**, *11*, 129−166.

(35) Zhu, B.; Shi, C.; Lin, M.; Ru, Y. Method for Oxidizing Isobutane. CN102757302B2015.

(36) Subramaniam, B.; Danby, A. M.; Lundin, M. D. Ozone-Facilitated Selective Oxidation of Alkanes in Liquid Carbon Dioxide. US10730814B2, 2017.

(37) Hellman, T. M.; Hamilton, G. A. Mechanism of Alkane Oxidation by Ozone in the Presence and Absence of Iron(III) Chloride. *J. Am. Chem. Soc.* **1974**, *96*, 1530−1535.

(38) Li, W.; Oyama, S. T. Catalytic Methane Oxidation at Low Temperatures Using Ozone. In *Heterogeneous Hydrocarbon Oxidation*, Warren, B. K.; Oyama, S. T., Eds.; 1996; vol. *638*, pp 364−373.

(39) Dardin, V. J.; Albright, L. F. Partial Oxidation of Propane Initiated by Ozone. *Ind. Eng. Chem. Proc. Design Dev.* **1965**, *4*, 61−66.

(40) Mytareva, A. I.; Mashkovsky, I. S.; Kanaev, S. A.; Bokarev, D. A.; Baeva, G. N.; Kazakov, A. V.; Stakheev, A. Y. Removal of VOCs by Ozone: *n*-Alkane Oxidation under Mild Conditions. *Catalysts* **2021**, *11*, 506−516.

(41) Timerghazin, Q. K.; Khursan, S. L.; Shereshovets, V. V. Theoretical study of the reaction between ozone and C−H bond: gas-phase reactions of hydrocarbons with ozone. *J. Mol. Struct.: THEOCHEM* **1999**, *489*, 87−93.

(42) Rotzoll, G. Mass spectrometric investigation of the *i*-C_4H_{10}−O_2−O_3 reaction and implications for the reaction mechanism. *Combust. Flame* **1987**, *69*, 229−233.

(43) Liu, J.; Yu, R.; Ma, B. Effect of Ozone Addition on the Cool Flame and Negative Temperature Coefficient Regions of Propane−Oxygen Mixtures. *ACS Omega* **2020**, *5*, 16448−16454.

(44) Caprio, V.; Insola, A.; Lignola, P. G. Ozone Activated Low Temperature Combustion of Propane in a C.S.T.R. *Combust. Sci. Technol.* **1983**, *35*, 215−224.

(45) Caprio, V.; Insola, A.; Lignola, P. G. Gas Phase Oxidation of *n*-Butane by Means of Ozonized Oxygen. *Combust. Sci. Technol.* **1979**, *20*, 19−24.

(46) Briner, E.; Carceller, J. Recherches sur le ròle de l'ozone comme catalyseur d'oxydation. VIII. — Ozonation du propane et du butane. *Helv. Chim. Acta* **1935**, *18*, 973−981.

(47) Borodin, A. A.; Razumovskii, S. D. On the Mechanism of the Reaction Between Ozone and Alcohols: Ozonation Kinetics of Butanol-1 and Its Esters in CCl_4. *Kinet. Catal.* **2009**, *50*, 385−389.

(48) Rakovsky, S.; Cnachkov, M.; Belitskii, M.; Zaikov, G. Kinetics and Mechanism of the Ozone Reaction with Alcohols, Ketones, Ethers and Hydroxybenzenes. *Chem. Chem. Technol.* **2016**, *10*, 531−551.

(49) Rakovsky, S. K.; Cherneva, D. R.; Deneva, M. Ozone Reactions with Aliphatic Ethers in CCl_4. Kinetics and Mechanism. *Int. J. Chem. Kinet.* **1995**, *27*, 153−165.

(50) Brabets, R.; Clark, D.; Snelson, A. Solubility of Ozone in Some Fluorocarbon Solvents. *J. Fluor. Chem.* **1988**, *41*, 311−320.

(51) Gromadzka, K.; Swietlik, J. Organic Micropollutants Degradation in Ozone-Loaded System with Perfluorinated Solvent. *Water Res.* **2007**, *41*, 2572−2580.

(52) Stich, F. A.; Bhattacharyya, D. Ozonolysis of Organic Compounds in a Two-Phase Fluorocarbon-Water System. *Environ. Prog.* **1987**, *6*, 224−229.

(53) Rusch, G. M. The Development of Environmentally Acceptable Fluorocarbons. *Crit. Rev. Toxicol.* **2018**, *48*, 615−665.

(54) Krasner, S. W.; Weinberg, H. S.; Richardson, S. D.; Pastor, S. J.; Chinn, R.; Sclimenti, M. J.; Onstad, G. D.; Thruston, A. D. Occurrence of a New Generation of Disinfection Byproducts. *Environ. Sci. Technol.* **2006**, *40*, 7175−7185.

(55) Sehested, K.; Holcman, J.; Bjergbakke, E.; Hart, E. J. Ozone Decomposition in Aqueous Acetate Solutions. *J. Phys. Chem. A* **1987**, *91*, 2359−2361.

(56) Subramaniam, B. Gas-Expanded Liquids for Sustainable Catalysis and Novel Materials: Recent Advances. *Coord. Chem. Rev.* **2010**, *254*, 1843−1853.

(57) Lundin, M. D.; Danby, A. M.; Akien, G. R.; Binder, T. P.; Busch, D. H.; Subramaniam, B. Liquid CO_2 as a Safe and Benign Solvent for the Ozonolysis of Fatty Acid Methyl Esters. *ACS Sustainable Chem. Eng.* **2015**, *3*, 3307−3314.

(58) Panich, N. M.; Ershov, B. G. Optical Properties and Solubility of Ozone in CCl_4 at Low Temperature. *Russ. J. Gen. Chem.* **2018**, *88*, 1071−1075.

(59) Rodríguez-Peña, M.; Barrios Pérez, J. A.; Llanos, J.; Sáez, C.; Rodrigo, M. A.; Barrera-Díaz, C. E. New Insights about the Electrochemical Production of Ozone. *Curr. Opin. Electrochem.* **2021**, *27*, 100697.

(60) Bailey, P. S. The Reactions of Ozone with Organic Compounds. *Chem. Rev.* **1958**, *58*, 925−1010.

(61) Khalizov, A. F.; Khursan, S. L.; Shereshovets, V. V. Free-radical Chain Decomposition of Ozone Initiated by Di(*tert*-butyl) Trioxide. *Russ. Chem. Bull.* **2001**, *50*, 63−67.

(62) Khursan, S. L. Peroxide Intermediates of Oxidation Processes: Organic Trioxides. *PATAI'S Chemistry of Functional Groups* **2009**, 1−72.

(63) Staehelin, J.; Hoigne, J. Decomposition of Ozone in Water: Rate of Initiation by Hydroxide Ions and Hydrogen Peroxide. *Environ. Sci. Technol.* **1982**, *16*, 676−681.

(64) Staehelin, J.; Hoigne, J. Decomposition of Ozone in Water in the Presence of Organic Solutes Acting as Promoters and Inhibitors of Radical Chain Reactions. *Environ. Sci. Technol.* **1985**, *19*, 1206−1213.

(65) Plesničar, B.; Cerkovnik, J.; Tekavec, T.; Koller, J. ^{17}O NMR Spectroscopic Characterization and the Mechanism of Formation of Alkyl Hydrotrioxides (ROOOH) and Hydrogen Trioxide (HOOOH) in the Low-Temperature Ozonation of Isopropyl Alcohol and Isopropyl Methyl Ether: Water-Assisted Decomposition. *Chem.-Eur. J.* **2000**, *6*, 809−819.

(66) Sun, Y.; Ni, L.; Papadaki, M.; Jiao, Z.; Zhu, W.; Jiang, J.; Mashuga, C.; Mannan, M. S.; Wilhite, B. Reaction Hazard and Mechanism Study of H_2O_2 Oxidation of 2-Butanol to Methyl Ethyl Ketone Using DSC, Phi-TEC II and GC-MS. *J. Loss Prev. Process Ind.* **2020**, *66*, 104177.

(67) Chhikara, B. S.; Chandra, R.; Tandon, V. A Versatile Method for the Hydrogen Peroxide Oxidation of Alcohols Using PTC Condition in *tert*-Butanol. *Synlett* **2005**, *2005*, 0872−0874.

(68) de Araújo, M. L.; Correia, G. A.; Carvalho, W. A.; Shul'pina, L. S.; Kozlov, Y. N.; Shul'pin, G. B.; Mandelli, D. The effect of additives (pyrazine, pyrazole and their derivatives) in the oxidation of 2-butanol with $FeCl_3$−H_2O_2 in aqueous solutions. *Catal. Today* **2021**, *381*, 163−170.

(69) Strle, G.; Cerkovnik, J. A Simple and Efficient Preparation of High-Purity Hydrogen Trioxide (HOOOH). *Angew. Chem., Int. Ed.* **2015**, *54*, 9917−9920.

(70) Klemola, K. T.; Ilme, J. K. Distillation Efficiencies of an Industrial-Scale *i*-Butane/*n*-Butane Fractionator. *Ind. Eng. Chem. Res.* **1996**, *35*, 4579−4586.

(71) Liu, N.; Qiu, N.; Li, Z.; Cai, C.; Shan, X.; Gao, T.; Wang, Y. Significance and Evolution Characteristics of the Isobutane/*n*-Butane Ratio of Natural Gas. *Energy Explor. Exploit.* **2020**, *38*, 494−518.

(72) Schreck, A.; Knorr, A.; Wehrstedt, K. D.; Wandrey, P. A.; Gmeinwieser, T.; Steinbach, J. Investigation of the Explosive Hazard of Mixtures Containing Hydrogen Peroxide and Different Alcohols. *J. Hazard. Mater.* **2004**, *108*, 1−7.

(73) Whiting, M. C.; Bolt, A. J. N.; Parish, J. H. The Reaction Between Ozone and Saturated Compounds. In *Oxidation of Organic Compounds*, American Chemical Society, 1968; Vol. *77*, pp 4−14.

(74) Razumovskii, S. D. Comparison of Reaction Rates for Ozone-Alkene and Ozone-Alkane Systems in the Gas Phase and in Solution. *Russ. Chem. Bull.* **1995**, *44*, 2287−2288.

(75) Shereshovets, V. V.; Galieva, F. A.; Akhunov, I. R.; Komissarov, V. D.; Tsar'kov, A. V.; Bikbulatov, I. K. Kinetics of Oxidation of

Monohydric Aliphatic Alcohols by Ozone. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1983**, *32*, 914−918.

(76) He, C.; You, F. Shale Gas Processing Integrated with Ethylene Production: Novel Process Designs, Exergy Analysis, and Techno-Economic Analysis. *Ind. Eng. Chem. Res.* **2014**, *53*, 11442−11459.

(77) *Natural Gas Liquids Primer with a Focus on the Appalachian Region*; U.S. Department of Energy: Washington, DC, 2017.

(78) Batakliev, T.; Georgiev, V.; Anachkov, M.; Rakovsky, S.; Zaikov, G. E. Ozone Decomposition. *Interdiscip. Toxicol.* **2014**, *7*, 47−59.

(79) Michael, J. V. Thermal Decomposition of Ozone. *J, Chem. Phys.* **1971**, *54*, 4455−4459.

(80) Jodzis, S.; Baran, K. The Influence of Gas Temperature on Ozone Generation and Decomposition in Ozone Generator. How Is Ozone Decomposed? *Vacuum* **2022**, *195*, 110647.

(81) Cerkovnik, J.; Eržen, E.; Koller, J.; Plesničar, B. Evidence for HOOO Radicals in the Formation of Alkyl Hydrotrioxides (ROOOH) and Hydrogen Trioxide (HOOOH) in the Ozonation of C−H Bonds in Hydrocarbons. *J. Am. Chem. Soc.* **2002**, *124*, 404−409.

(82) Shereshovets, V. V.; Khursan, S. L.; Komissarov, V. D.; Tolstikov, G. A. Organic Hydrotrioxides. *Russ. Chem. Rev.* **2001**, *70*, 105−129.

(83) Gambo, Y.; Adamu, S.; Abdulrasheed, A. A.; Lucky, R. A.; Ba-Shammakh, M. S.; Hossain, M. M. Catalyst Design and Tuning for Oxidative Dehydrogenation of Propane − A Review. *Appl. Catal., A* **2021**, *609*, 117914.

(84) Denisov, E. T.; Afanas'ev, I. B. Chain Mechanism of Liquid-Phase Oxidation of Hydrocarbons. *Oxidation and Antioxidants in Organic Chemistry and Biology*, CRC Press, 2005; pp 21−82.

(85) Gerchikov, A. Y.; Zimin, Y. S.; Trukhanova, N. V.; Evgrafov, V. N. Kinetics of Oxidation of Aliphatic Alcohols by Ozone in Aqueous Solutions. *React. Kinet. Catal. Lett.* **1999**, *68*, 257−263.

(86) Zheng, W.; Jewitt, D.; Kaiser, R. I. Mechanistical studies on the formation of isotopomers of hydrogen peroxide (HOOH), hydrotrioxy (HOOO), and dihydrogentrioxide (HOOOH) in electron-irradiated $H_2{}^{18}O/O_2$ ice mixtures. *Phys. Chem. Chem. Phys.* **2007**, *9*, 2556−2563.

(87) Anglada, J. M.; Martins-Costa, M.; Francisco, J. S.; Ruiz-López, M. F. Interconnection of Reactive Oxygen Species Chemistry across the Interfaces of Atmospheric, Environmental, and Biological Processes. *Acc. Chem. Res.* **2015**, *48*, 575−583.

(88) Fischbacher, A.; von Sonntag, J.; von Sonntag, C.; Schmidt, T. C. The •OH Radical Yield in the $H_2O_2 + O_3$ (Peroxone) Reaction. *Environ. Sci. Technol.* **2013**, *47*, 9959−9964.

(89) Merényi, G.; Lind, J.; Naumov, S.; von Sonntag, C. Reaction of Ozone with Hydrogen Peroxide (Peroxone Process): A Revision of Current Mechanistic Concepts Based on Thermokinetic and Quantum-Chemical Considerations. *Environ. Sci. Technol.* **2010**, *44*, 3505−3507.

(90) Gallo, A., Jr.; Musskopf, N. H.; Liu, X.; Yang, Z.; Petry, J.; Zhang, P.; Thoroddsen, S.; Im, H.; Mishra, H. On the formation of hydrogen peroxide in water microdroplets. *Chem. Sci.* **2022**, *13*, 2574−2583.

(91) Koppenol, W. H.; Stanbury, D. M.; Bounds, P. L. Electrode potentials of partially reduced oxygen species, from dioxygen to water. *Free Radic. Biol. Med.* **2010**, *49*, 317−322.