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Functional Group Chemistry of Low-Temperature Biofuel Oxidation

Brandon Rotavera[1, 2,*], *Craig A. Taatjes*[3]

[1]*College of Engineering, University of Georgia, Athens, GA, USA*
[2]*Department of Chemistry, University of Georgia, Athens, GA, USA*
[3]*Combustion Chemistry Department, Sandia National Laboratories, Livermore, CA, USA*
[*]*Corresponding Author Email: rotavera@uga.edu*

Abstract: Because of the structural diversity in biofuels, owing to functional groups such as ethers (R–O–R), alcohols (R–OH), carbonyls (R–C(=O)–R), and esters (R–C(=O)–C–O–R), peroxy radical-driven reaction mechanisms that underpin chain-branching chemistry are dependent heavily on molecular structure. Labile hydrogen atoms, enhanced ring-opening reaction rates, and the influence of resonance-stabilization are some of the characteristics that functional groups impose. The impact on autoignition chemistry arises from alterations in initial radical distributions as well as $\dot{R} + O_2$ reaction pathways relative to analogous alkane species. The present work provides a concise review of low-temperature oxidation chemistry of cyclic ethers with an emphasis on autoignition.

Keywords: biofuel, QOOH, peroxy radicals, autoignition, chemical kinetics

1. Introduction

Understanding low-temperature oxidation of cyclic ethers is relevant to two areas of combustion chemistry. In addition to providing utility as advanced biofuels, cyclic ethers are also intermediates in low-temperature alkane oxidation, formed coincident with $\dot{O}H$ in a chain-propagating step via unimolecular QOOH decomposition. Figure 1 shows the molecular structure of four representative cyclic ethers: tetrahydrofuran, 2-methyltetrahydrofuran, 3-methyltetrahydrofuran, and tetrahydropyran. The presence of the ether group in the ring creates distinct H-abstraction sites, e.g. α, β , and γ; prime notation in Figure 1 reflects α carbon on the side of the ring where the substituent is located. The C–H bond dissociation energy on secondary α carbon is lowered by approximately 4 – 5 kcal/mol relative to secondary carbon in alkanes [1-4]. For tertiary α' carbon, as in Figure 1b, the effect is smaller: ca. 2 kcal/mol [3-5]. However, unlike in ketones or ethers where the carbonyl group introduces resonance stabilization into initial α radicals, the well-depth of the adduct from $\dot{R} + O_2$ reactions in ethers is similar to that of alkylperoxy radicals (ca. 36 kcal/mol) [2]. The net effect of the –O– group on initiation reactions is a reduction in the C–H bond energy of α carbon, which results in a favoring of initial α radicals formed via abstraction by $\dot{O}H$ and $HO\dot{O}$, among other radicals. Subsequent reactions of α radicals is therefore expected to play a predominant role in oxidation reactions of cyclic ethers.

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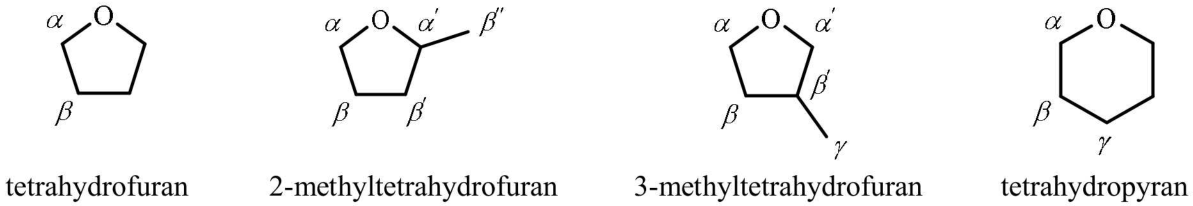

Figure 1: Molecular structures of cyclic ethers with H-abstraction sites labeled. The –O– group reduces C–H bond energy on adjacent carbon (α and α') by approximately 4 – 5 kcal/mol relative to secondary carbon in alkanes [1-4].

2. Low-Temperature Oxidation of Cyclic Ethers

Low-temperature chain-branching in hydrocarbons and biofuels stems from a degenerate chain-branching mechanism initiated by the addition of O_2 to an organic radical, $\dot{R}$. Subsequent isomerization of organic peroxy radicals, $RO\dot{O}$, to carbon-centered hydroperoxyalkyl, QOOH, followed by a second O_2-addition step ($QOOH + O_2 \rightarrow \dot{O}OQOOH$) leads to chain-branching, the process responsible for multiplying reactive radicals causing accelerated combustion reactions leading to autoignition and accompanying heat release rates.

Comprehensive chemical kinetics models used in the simulation of hydrocarbon and biofuel oxidation rely on accurate prescription of the underlying reaction mechanisms and rate parameters of associated elementary reactions. Such models contain thousands of elementary reactions, which collectively define chain-initiation, -propagation, -branching, and -inhibition pathways. In the low-temperature regime, below approximately 1000 K where $\dot{R} + O_2$ reactions dominate, cyclic ethers are primary oxidation intermediates of hydrocarbon oxidation that are formed in abundance via unimolecular decomposition of either chemically activated or thermalized radicals, i.e. $RO\dot{O}$ or QOOH. In addition, several cyclic ethers are potential biofuels, including tetrahydrofuran, 2- and 3-methyltetrahydrofuran, and tetrahydropyran, which undergo unique peroxy radical chemistry due to the presence of the functional group.

2.1. tetrahydrofuran

Stoichiometric ignition delay time simulations were conducted on tetrahydrofuran using the mechanism of [6] and compared to cyclopentane [7] at an initial pressure of 20 atm and with an N_2 mole fraction of ~0.76 (Figure 2). In both cases, ignition was defined using the method of steepest ascent [8] applied to $\dot{O}H$ time histories modeled using a dP/dt of 3%/ms in the 0D homogeneous reactor module in ChemKin. While negative temperature coefficient behavior, which is indicative of peroxy radical-mediated chemistry, is evident in cyclopentane and negligible in tetrahydrofuran, model-predicted ignition delay times for the cyclic ether are $\sim 10^1$ shorter than for the cycloalkane below ~800 K. The substantial difference suggests that reactions via second O_2-addition reactions are comparatively facile in tetrahydrofuran and, in addition, raises the question as to the contribution from products formed via $\dot{R}$ or QOOH ring-opening [9] to chain-branching. Measurements of tetrahydrofuran ignition delay times include high-pressure shock tube experiments in Uygun et al [10], conducted from 691 – 1100 K and at two pressures, 20 and 40 atm, and the RCM experiments of Vanhove et al. [11], conducted from 640 – 900 K and at 5 and 10 atm. The 20-atm results from [10] and [11] are plotted in Figure 2b and display similar trends to the simulations.

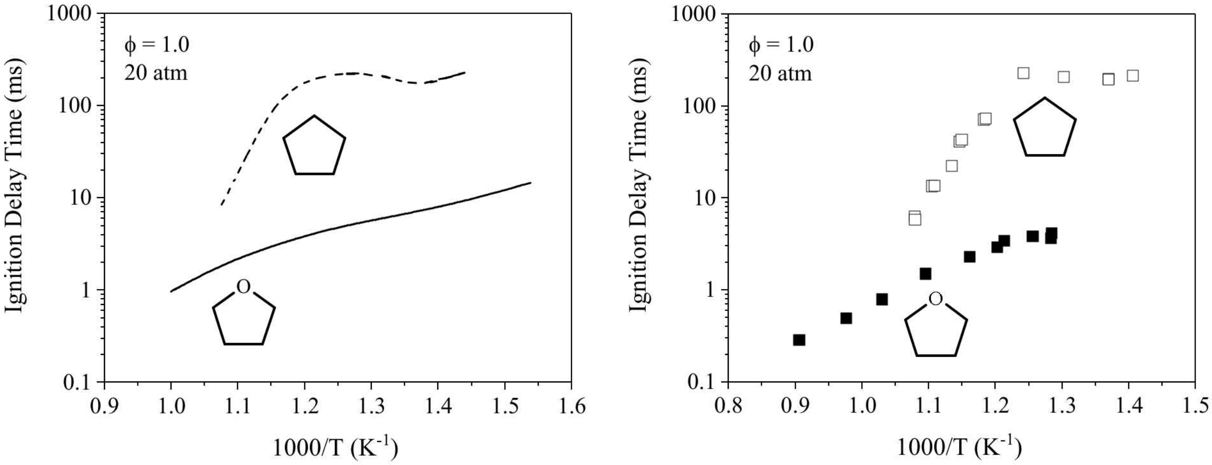

Figure 2: (a) Comparison of ignition delay time simulations of tetrahydrofuran [6] and cyclopentane [7]. 20 atm, $\phi = 1.0$. N_2 mole fraction ~0.76. (b) Stoichiometric ignition delay times at 20 atm of tetrahydrofuran [10] cyclopentane [7].

2.2. 2-methyltetrahydrofuran and 3-methyltetrahydrofuran

Tripathi et al. [12] report shock tube and RCM ignition delay time measurements, conducted at high pressure (10 – 40 bar) over 625 – 1250 K, and developed the first chemical kinetics model for 3-methyltetrahydrofuran oxidation. Because of the reduction in C–H bond energy, H-abstraction by $\dot{O}H$ at low temperature primarily occurs on α carbon (~75%) followed by abstraction from tertiary β' and secondary β carbon (both ~10%). Abstraction from the $-CH_3$ group is of minor importance. To a larger extent than in 2-methyltetrahydrofuran [13], the model predictions indicate that ring-opening reactions of initial α radicals in 3-methyltetrahydrofuran are competitive with O_2-addition at temperatures below 750 K and ultimately become favored with increasing temperature.

The results were compared to 2-methyltetrahydrofuran [5] and confirmed that low-temperature chain-branching, below 750 K, is more pronounced in 3-methyltetrahydrofuran, which is consistent with the RCM measurements of Sudholt et al. [3]. Ignition delay time differences of ~10^1 ms were observed in both the experimental and modeling results. Effectively, the location of the methyl group α to the ether group restricts the degree to which low-temperature chain-branching is promoted because of the lack of availability of hydrogen atoms for the isomerization step preceding ketohydroperoxide formation: $\dot{O}OQOOH \rightarrow HOOQOOH$. In the case of 2-methyltetrahydrofuran where the –OOH group is in the α' position (cf. Figure 1), no hydrogen remains for abstraction because of the presence of the methyl group on the same carbon.

Stoichiometric ignition delay times simulations were conducted on tetrahydrofuran, 2- and 3-methyltetrahydrofuran using the chemical kinetics mechanisms of Fenard et al. [6], Tripathi et al. [5], and Tripathi et al. [12], respectively at an initial pressure of 20 atm and with an N_2 mole fraction of ~0.76 (Figure 3). In both cases, ignition was defined using the method of steepest ascent [8] applied to $\dot{O}H$ time histories modeled using a dP/dt of 3%/ms in the 0D homogeneous reactor module in ChemKin. The comparison highlights the effect of methyl substitution on tetrahydrofuran ignition chemistry. In part, as noted in [12], the longer ignition delay times in 3-

methyltetrahydrofuran is due to the lack of available hydrogen in α radicals for abstraction in $\dot{O}$OQOOH isomerization reactions. In contrast, in the case of 2-methyltetrahydrofuran, four such abstraction sites are present as is a tertiary C–H bond.

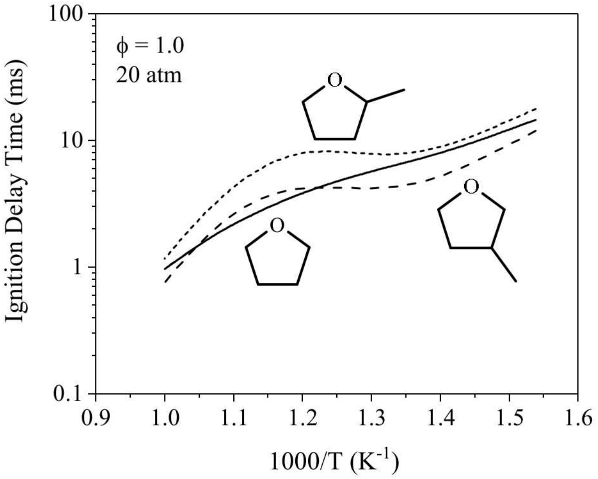

Figure 3: Simulated ignition delay times of tetrahydrofuran (Fenard et al. [6]), 2-methyltetrahydrofuran (Tripathi et al. [5]), and 3-methyltetrahydrofuran (Tripathi et al. [12]). ϕ = 1.0 and 20 atm. N_2 mole fraction ~0.76.

2.3. tetrahydropyran

Rotavera et al. [2] employed MPIMS experiments to determine the influence of the ether group in tetrahydropyran on chain-termination in comparison to cyclohexane. Below 700 K and 10 Torr, chain-termination is more favorable in tetrahydropyran due to coupled effects of (1) lower C–H bond energy of the α-carbon, which leads to α-tetrahydropyranyl being the dominant initial radical, and (2) the barrier to direct HO$\dot{O}$ formation on the α-tetrahydropyranyl + O_2 surface being lower by approximately 5 kcal/mol. With increasing temperature, however, competition from α-tetrahydropyranyl ring-opening reduces the flux through $\dot{R}$ + O_2 and subsequent product formation thereafter – an effect compounded by the fact that abstraction at the weakest C–H bond produces the initial radical most amenable to ring-opening.

Davis et al. [14] conducted MPIMS on cyclohexane and tetrahydropyran at two pressures (10 Torr and 1520 Torr) and three temperatures (500 K, 600 K, and 700 K). Branching fractions measurements indicated that product formation from unimolecular decomposition of QOOH radicals via concerted C–C and C–O β-scission were more pronounced in tetrahydropyran oxidation than in cyclohexane oxidation, which in the case of the former above 675 K prevents QOOH + O_2 reactions that are necessary for ketohydroperoxide formation. Figure 4 shows the temperature dependence of ion signal at *m/z* 132, which corresponds to the mass-to-charge ratio of ketohydroperoxide isomers formed in tetrahydropyran oxidation. Similar to alkane oxidation [15, 16], peak formation occurs near 625 K. In contrast to cyclohexane [14], however, temperatures above 650 K suppress the chain reaction sequence leading to $\dot{O}$OQOOH and subsequently to ketohydroperoxide.

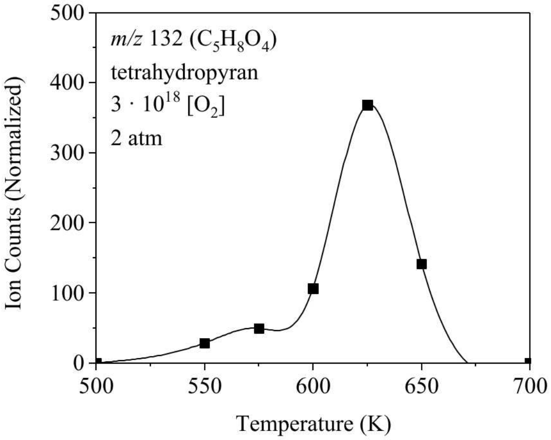

Figure 4: Laser-shot-normalized integrated ion counts for *m/z* 132 in tetrahydropyran oxidation indicating peak ketohydroperoxide formation at 625 K.

The main conclusion drawn from the temperature dependence of the *m/z* 132 signal relates to the importance ring-opening pathways for both Ṙ and QOOH radicals are relevant in tetrahydropyran oxidation and not in cyclohexane. In the former case, the ether group promotes pathways that diminish the already low steady-state concentration of QOOH. Four pathways connected to the depletion of QOOH in tetrahydropyran were postulated in Davis et al. [14]: (i) γ-QOOH → pentanedial + ȮH, (ii) γ-QOOH → vinyl formate + ethene + ȮH, (iii) γ-QOOH → 3-butenal + formaldehyde + ȮH, and (iv) β-QOOH → acrolein + oxirane + ȮH. Carbon balance calculations revealed that products from ring-opening from both Ṙ and QOOH, at 700 K, account for > 70% at 10 Torr and > 55% at 1520 Torr. Analogous mechanisms in cyclohexane oxidation leading to similar intermediates are defined, and on the basis of mass spectra results confirm that such ring-opening reactions are non-existent.

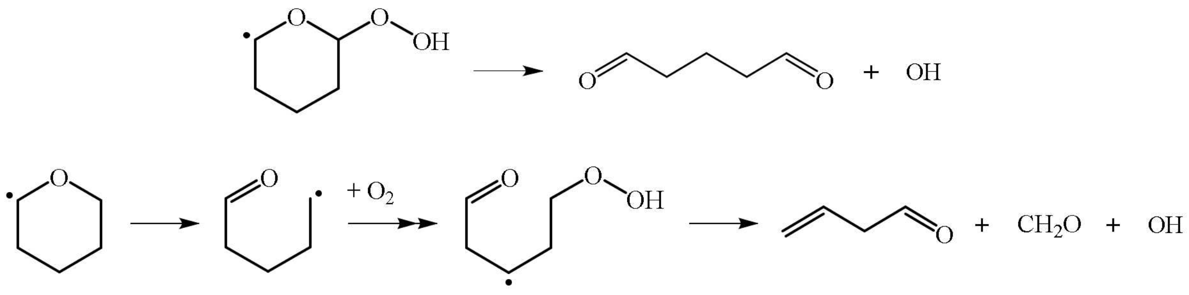

Figure 5: Ring-opening pathways in tetrahydropyran oxidation

Three chemical kinetics mechanisms exist for tetrahydropyran (Dagaut et al. [17], Labbe et al. [18], and Tran et al. [19]). However, none include peroxy radical chemistry and no ignition delay time measurements are reported below 1000 K [17], unlike cyclohexane [20, 21]. An open question therefore remains as to the effect of the ether group on ignition delay times in the oxidation of a 6-membered ring.

3. Conclusions

The present work provides a concise review on the autoignition chemistry of cyclic ethers, which indicates that peroxy radical chemistry differs substantially compared to alkanes. In large part, ring-opening reactions leading to smaller, partially oxidized radicals during the incipient oxidation steps are responsible for creating complex chemistry at temperatures below 1000 K. Because of the importance to sub-mechanisms in comprehensive chemical kinetics models of alkane oxidation and to utilization as biofuels, detailed understanding of low-temperature combustion chemistry of cyclic ethers using both theory and experiment remains a significant target.

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5. References

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