Formation and Atmospheric Reactions of 4,5-Dihydro-2-methylfuran

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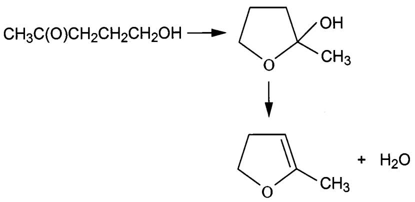
4,5-Dihydro-2-methylfuran (DHMF) can be formed from cyclization of 5-hydroxy-2-pentanone, an important gas-phase photooxidation product of *n*-pentane and a representative 1,4-hydroxycarbonyl. At very low ($\ll$1%) relative humidity a lifetime of ~1.1 h was obtained for the transformation of 5-hydroxy-2-pentanone to DHMF. Rate constants and products of the gas-phase reactions of DHMF with OH radicals, NO_3 radicals, and ozone have been determined at 298 ± 2 K and atmospheric pressure of air using in situ Fourier transform infrared (FT-IR) spectroscopy, in situ atmospheric pressure ionization tandem mass spectrometry (API-MS/MS), and combined gas chromatography−mass spectrometry (GC−MS). Rate constants (in cm^3 $molecule^{-1}$ s^{-1}) for the reactions of DHMF with OH radicals, NO_3 radicals, and O_3 were measured to be $(2.18 \pm 0.11) \times 10^{-10}$, $(1.68 \pm 0.12) \times 10^{-10}$, and $(3.49 \pm 0.24) \times 10^{-15}$, respectively, resulting in estimated tropospheric lifetimes of 1.3 h, 24 s, and 7 min for the OH radical, NO_3 radical, and O_3 reactions, respectively. The yields of identifiable products from the atmospheric reactions of DHMF were quantified, and possible mechanisms for their formation are discussed.

Introduction

In the troposphere, the dominant loss process for alkanes is by reaction with the hydroxyl (OH) radical.[1] In the presence of NO, the OH radical initiated reactions of alkanes lead to formation of alkoxy (RO•) radical intermediates which subsequently decompose, react with O_2, and isomerize,[1,2] with the isomerization reactions being predicted to generally result in the formation of 1,4-hydroxycarbonyls.[1−3] Consistent with these predictions, product studies of the reactions of C_4–C_8 *n*-alkanes with the OH radical in the presence of NO show that hydroxycarbonyls account for a significant fraction of the overall reaction products.[4−9] Eberhard et al.[4] used combined gas chromatography−mass spectrometry to identify and quantify 5-hydroxy-2-hexanone as its 2,4-diphenylhydrazone derivative from the OH radical initiated reaction of *n*-hexane in the presence of NO, as well as from the 2-hexoxy radical produced by the photolysis of 2-hexyl nitrite. Previous studies from this laboratory[5−9] using in situ atmospheric pressure ionization tandem mass spectrometry (API-MS) have shown that hydroxycarbonyls account for significant, and often dominant, fractions of the total products formed from $>C_4$ alkanes, with the remaining products being alkyl nitrates, 1,4-hydroxyalkyl nitrates, and carbonyl compounds. For example, hydroxycarbonyls (presumed to be 1,4-hydroxycarbonyls) account for ~30−50% of the products formed from the OH radical initiated reactions of *n*-pentane through *n*-octane.[7]

The only commercially available 1,4-hydroxycarbonyl is 5-hydroxy-2-pentanone, which in the liquid phase is reported to be in equilibrium with its cyclic hemiacetal form.[10] Formation of 4,5-dihydro-2-methylfuran from 5-hydroxy-2-pentanone by thermal dehydration in the liquid phase[11,12] and by catalytic dehydration in the gas phase[13] has been reported. In previous studies, both in this laboratory and by Cavalli et al.,[14] vapor-phase samples of 5-hydroxy-2-pentanone introduced into environmental chambers have been observed to convert at an appreciable rate at room temperature to 4,5-dihydro-2-methylfuran, most likely via loss of a water molecule from the cyclic hemiacetal.



In this work we have investigated the conversion of 5-hydroxy-2-pentanone to 4,5-dihydro-2-methylfuran (DHMF) and studied the atmospherically relevant reactions of DHMF with OH radicals, NO_3 radicals, and O_3.

Experimental Methods

Kinetic Studies. Experiments were carried out at 298 ± 2 K in a 5870 L evacuable, Teflon-coated chamber equipped with an in situ multiple-reflection optical system interfaced to a Nicolet 7199 FT-IR spectrometer. Irradiation was provided by a 24-kW xenon arc lamp, with the light being filtered through a 6 mm thick Pyrex pane to remove wavelengths <300 nm. The chamber is fitted with two Teflon-coated fans to ensure rapid mixing of reactants during their introduction into the chamber. IR spectra were recorded with 64 scans per spectrum (corresponding to 2.0 min averaging time), a full-width-at-half-maximum resolution of 0.7 cm^{-1}, and a path length of 62.9 m.

Rates of conversion of 5-hydroxy-2-pentanone to 4,5-dihydro-2-methylfuran were measured at 298 ± 2 K and at ~1.5, 16,

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and 740 Torr total pressure of dry N_2. Rate constants for the reactions of OH and NO_3 radicals and O_3 with 4,5-dihydro-2-methylfuran were measured at 298 ± 2 K and 740 Torr total pressure of dry synthetic air (80% N_2 + 20% O_2), using relative rate techniques in which the reactions of 4,5-dihydro-2-methylfuran and a reference compound were monitored in the presence of OH radicals, NO_3 radicals, or O_3.

$$\left.\begin{array}{l}\mathrm{OH}\\ \mathrm{NO_3}\\ \mathrm{O_3}\end{array}\right\} + \text{4,5-dihydro-2-methylfuran} \rightarrow \text{products} \qquad (1)$$

$$\left.\begin{array}{l}\mathrm{OH}\\ \mathrm{NO_3}\\ \mathrm{O_3}\end{array}\right\} + \text{reference compound} \rightarrow \text{products} \qquad (2)$$

Providing that 4,5-dihydro-2-methylfuran (DHMF) and the reference compound react only with OH radicals, NO_3 radicals, or O_3, then

$$\ln\left(\frac{[\mathrm{DHMF}]_{t_0}}{[\mathrm{DHMF}]_t}\right) = \frac{k_1}{k_2}\ln\left(\frac{[\text{ref compd}]_{t_0}}{[\text{ref compd}]_t}\right) \qquad (\mathrm{I})$$

where $[\mathrm{DHMF}]_{t_0}$ and $[\text{ref compd}]_{t_0}$ are the concentrations of 4,5-dihydro-2-methylfuran and reference compound at time t_0, $[\mathrm{DHMF}]_t$ and $[\text{ref compd}]_t$ are the corresponding concentrations at time t, and k_1 and k_2 are the rate constants for reactions 1 and 2, respectively.

Hydroxyl radicals were generated in the presence of NO by the photolysis of CH_3ONO in air[15] at wavelengths >300 nm. The initial reactant concentrations employed for the OH radical reaction were 2.5 × 10^{14} molecules cm^{-3} each of DHMF, the reference compound (cyclohexene or 2-methylpropene), CH_3ONO, and NO. Irradiations were carried out intermittently, with IR spectra being recorded during the dark periods and with total irradiation times of 7−8 min. NO_3 radicals were generated in situ in the dark by the thermal decomposition of N_2O_5,[16,17] and O_3 was produced as O_3/O_2 mixtures of known concentrations by an ozone generator. For both the NO_3 radical and O_3 reactions, the initial reactant concentrations (molecules cm^{-3}) were the following: DHMF, 2.5 × 10^{14}; and 2,3-dimethyl-2-butene (the reference compound), 4.9 × 10^{14}; with successive additions of aliquots of N_2O_5 [three to four additions of (0.93−1.2) × 10^{14} molecules cm^{-3} N_2O_5 in the chamber] or O_3 [three to four additions of (0.79−1.1) × 10^{14} molecules cm^{-3} O_3 in the chamber] and with the aliquots being added after complete consumption of the previously added N_2O_5 or O_3. The O_3 experiments were carried out in the presence of 1.6 × 10^{17} molecules cm^{-3} of cyclohexane, sufficient to scavenge ≥90% of the OH radicals formed.[1,3]

In addition, DHMF concentrations were monitored in DHMF−air mixtures, both in the dark under dry conditions (≪1% relative humidity) and in the presence of 4.0 × 10^{16} molecules cm^{-3} water vapor (5% relative humidity), and during irradiation. The initial DHMF concentrations were the same as those used in the kinetic experiments.

Product Studies. Experiments were carried out at 298 ± 2 K and 740 Torr total pressure of air in three reaction chambers: in the 5870 L evacuable chamber with in situ FT-IR analysis, in a 7900 L Teflon chamber equipped with two parallel banks of black lamps and interfaced to a PE SCIEX API III MS/MS direct air sampling, atmospheric pressure ionization tandem mass spectrometer (API-MS); and in a 7500 L Teflon chamber equipped with black lamps and with provision for sampling onto a Solid-Phase Micro Extraction (SPME) fiber.[18]

The majority of experiments carried out to identify the products of the reactions of DHMF were carried out in the 5870 L evacuable chamber with in situ FT-IR analyses. For the OH radical reactions, the initial concentrations (in units of 10^{14} molecules cm^{-3}) were CH_3ONO, 2.46; NO, 2.46; and DHMF, 0.74−2.46. To measure the yield of HCHO, one experiment employed 2-propyl nitrite instead of methyl nitrite as the OH radical precursor[19] [photolysis of 2-propyl nitrite forms acetone,[19] in contrast to the photolysis of methyl nitrite which forms HCHO], with initial concentrations (in units of 10^{14} molecules cm^{-3}) of $(CH_3)_2CHONO$, 1.47; NO, 2.46; and DHMF, 2.46.

One experiment was also carried out in the 7500 L all-Teflon chamber (at ∼1% relative humidity) with initial reactant concentrations (molecules cm^{-3}) of CH_3ONO, 2.4 × 10^{14}; NO, 1.9 × 10^{14}; and DHMF, 2.40 × 10^{13}. After irradiation for 1 min (corresponding to 15−20% reaction of DHMF based on similar experiments with other organic compounds), a 65 μm PDMS/DVB SPME fiber coated with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride[20] was exposed to the chamber contents for 3 min, and then analyzed by GC−MS with thermal desorption onto a 30 m DB-1701 fused silica capillary column in a Varian 2000 GC/MS with analysis by isobutane chemical ionization.

For the reaction with NO_3 radicals, one experiment was carried out in which 1.23 × 10^{14} molecules cm^{-3} N_2O_5 was added to 2.46 × 10^{14} molecules cm^{-3} DHMF in air. Two experiments were carried out for the reaction with O_3, with 8.5 × 10^{16} molecules cm^{-3} cyclohexane being present as an OH radical scavenger in one of the experiments. In each of these experiments, two separate aliquots of 1.29 × 10^{14} molecules cm^{-3} O_3 were added to the DHMF (2.46 × 10^{14} molecules cm^{-3})−air mixture.

Reactions of DHMF with OH radicals, NO_3 radicals, and O_3 were also carried out in the 7900 L Teflon chamber at 740 Torr of purified air at ∼5% relative humidity with API-MS and API-MS/MS analyses. The operation of the API-MS in the MS (scanning) and MS/MS [with collision activated dissociation (CAD)] modes has been described elsewhere.[21] The positive ion mode was used in these analyses, with protonated water hydrates $[H_3O^+(H_2O)_n]$ acting as the ionizing agent and resulting in the ions that were mass-analyzed being mainly protonated molecules ($[M + H]^+$) and their protonated homo- and heterodimers.[21] For the OH radical reactions, the initial reactant concentrations (in molecules cm^{-3}) were CH_3ONO and NO, (4.4−4.7) × 10^{13} each; and DHMF, 2.3 × 10^{13}. The mixtures were irradiated for 0.17−5.67 min at 20% of the maximum light intensity, with API-MS spectra being recorded prior to irradiation and after each irradiation. For the NO_3 reactions, the initial concentrations (molecules cm^{-3}) were DHMF, 2.3 × 10^{13}; NO_2 (added to slow the N_2O_5 decomposition), 2.2 × 10^{13}; and N_2O_5, 1.4 × 10^{13}. For the O_3 experiments, the initial concentrations (molecules cm^{-3}) were DHMF, 2.3 × 10^{13}; cyclohexane, 1.4 × 10^{16}. There were two additions of O_3, with each addition corresponding to an initial O_3 concentration of ∼5 × 10^{12} molecules cm^{-3} in the chamber.

Chemicals. The chemicals used and their stated purities were as follows: 5-hydroxy-2-pentanone (95%), TCI America; 4,5-dihydro-2-methylfuran [DHMF] (97%), 2-methylpropene (99%), 2,3-dimethyl-2-butene (99+%), Aldrich Chemical Co.; cyclohexene (99%), Chem Samples Co.; and NO (≥99%) and NO_2 (≥99.0%), Matheson Gas Products. Methyl nitrite was prepared

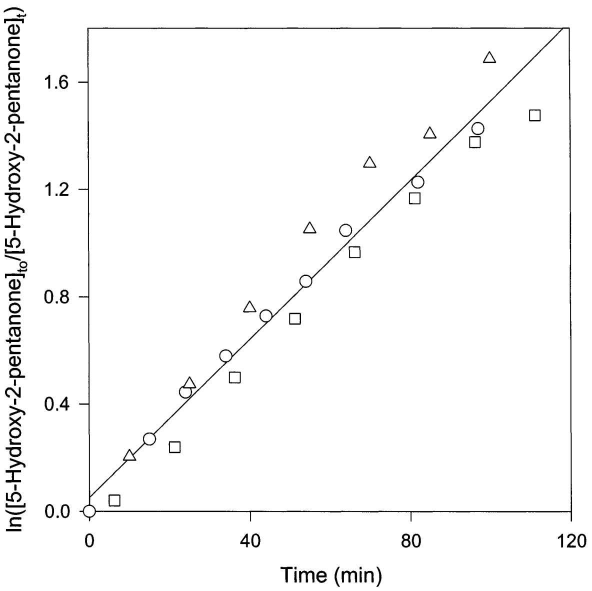


Figure 1. First-order plots of the decays of 5-hydroxy-2-pentanone in the 5870 L evacuable chamber at 1.5 (□), 16 (△), and 740 (○) Torr total pressure of dry N_2. The decay rates for the three experiments are, in chronological order, $(1.45 \pm 0.09) \times 10^{-2}$ min^{-1} at 740 Torr (the indicated errors are two least-squares standard deviations), $(1.48 \pm 0.05) \times 10^{-2}$ min^{-1} at 1.5 Torr, and (5 months later after numerous other types of reactions had been conducted in the chamber) $(1.68 \pm 0.13) \times 10^{-2}$ min^{-1} at 16 Torr. The line shown is from a least-squares analysis of the entire data set.

as described by Taylor et al.[22] and an analogous method was employed for the synthesis of 2-propyl nitrite. N_2O_5 was prepared by reacting NO_2 with O_3 as described by Atkinson et al.[16] Methyl nitrite, 2-propyl nitrite, and N_2O_5 were all stored at 77 K under vacuum prior to use. Partial pressures of all the above chemicals were measured in calibrated 2 and 5 L Pyrex bulbs with a 100-Torr MKS Baratron sensor, except for 5-hydroxy-2-pentanone, which was introduced into the bulbs with a microliter syringe, and flushed into the chambers with a stream of N_2 gas. Ozone was produced in a Welsbach T-408 ozone generator at precalibrated settings of voltage and input flow of high-purity O_2 (Puritan-Bennett Corp., 99.994%).

Results and Discussion

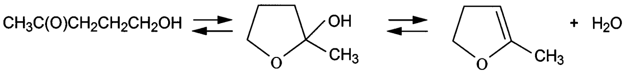
Kinetic Studies. *5-Hydroxy-2-pentanone Decays in Dry N_2.* In situ FT-IR analyses of mixtures of 2.48×10^{14} molecules cm^{-3} 5-hydroxy-2-pentanone in dry N_2 ($\ll$1% relative humidity) at total pressures of 1.5−740 Torr in the 5870 L evacuable chamber showed the formation of DHMF (8−18% of the 5-hydroxy-2-pentanone introduced) after the 12−20 min introduction and mixing period. For the experiment at ~1.5 Torr total pressure in which 5-hydroxy-2-pentanone was introduced (with a flow of N_2) into the evacuated chamber, the measured gas-phase concentration of 5-hydroxy-2-pentanone after the 12-min introduction period was only 40% of that introduced into the chamber, suggesting a significant loss of 5-hydroxy-2-pentanone (presumably to the walls). As shown in Figure 1, after the introduction and mixing periods the measured decays of 5-hydroxy-2-pentanone followed first-order behavior. In all three experiments, the sum of the concentrations of gas-phase 5-hydroxy-2-pentanone remaining and DHMF formed after ~100 min accounted for only 75−80% of the initial 5-hydroxy-2-pentanone (as measured after the introduction and mixing period).

Based upon these three experiments conducted over a period of several months, the 5-hydroxy-2-pentanone decay rate in dry N_2 was independent of the total pressure with a first-order rate constant of 1.5×10^{-2} min^{-1}. The lifetime of 5-hydroxy-2-pentanone in this chamber at low water vapor concentrations ($<8 \times 10^{15}$ molecules cm^{-3}) is therefore 1.1 h. A very similar decay rate (1.3×10^{-2} min^{-1}) and hence lifetime was reported by Cavalli et al.[14,23] for conversion of 5-hydroxy-2-pentanone to DHMF in a 480 L glass chamber in dry synthetic air.

Photolysis and Dark Decays of 4,5-Dihydro-2-methylfuran. Photolysis of DHMF in dry air showed ~1% loss of DHMF after 30 min irradiation, indicating that photolysis of DHMF during the OH radical reactions was negligible (<1%) and also that there was no significant decay of DHMF in dry air ($\leq 3 \times 10^{-4}$ min^{-1}). However, in the presence of 4.0×10^{16} molecules cm^{-3} water vapor (5% relative humidity), DHMF was observed to decay in the dark at a rate of $(4.8 \pm 0.2) \times 10^{-3}$ min^{-1} (as elsewhere in this article, the indicated error is two least-squares standard deviations), with a measured 58% loss of the initial DHMF over a period of 185 min and concurrent formation of 5-hydroxy-2-pentanone in ~92% yield (only an approximate quantification of 5-hydroxy-2-pentanone by FT-IR in the presence of water vapor could be obtained). No evidence for attainment of an equilibrium between DHMF and 5-hydroxy-2-pentanone was observed over this time scale.

Clearly, the kinetic and product studies conducted in dry air ($\ll$1% relative humidity) were for the reactions of OH radicals, NO_3 radicals, and O_3 with DHMF without interference from 5-hydroxy-2-pentanone. In contrast, in the presence of water vapor DHMF decays to form 5-hydroxy-2-pentanone with a measured DHMF lifetime at 5% relative humidity of 3.5 h. The forward and backward reactions shown in Scheme 1 therefore occur, leading in the presence of water vapor to interconversion of 5-hydroxy-2-pentanone and DHMF to some equilibrium ratio.

SCHEME 1



While the reactions of DHMF can be studied in dry air, it appears that the reactions of DHMF in the presence of water vapor are complicated by this interconversion, making unambiguous kinetic and product studies difficult. Indeed, it is possible that the API-MS analyses of the reaction of DHMF with OH radicals conducted at ~5% relative humidity involved the participation of 5-hydroxy-2-pentanone and/or its cyclized form (5-hydroxy-2-pentanone is not anticipated to react with O_3 at a measurable rate and the reaction of NO_3 radicals with 5-hydroxy-2-pentanone is expected to be approximately 5 orders of magnitude slower than with DHMF[24]).

Rate Constants for Reactions of 4,5-Dihydro-2-methylfuran. The data obtained from irradiations of CH_3ONO−NO−DHMF−cyclohexene−air and CH_3ONO−NO−DHMF−2-methylpropene−air mixtures are plotted in accordance with eq I in Figure 2, and the data from reacting N_2O_5−NO_3−NO_2−DHMF−2,3-dimethyl-2-butene−air and O_3−DHMF−2,3-dimethyl-2-butene−cyclohexane (in excess)−air mixtures are shown in analogous plots in Figure 3. Good straight-line plots are observed, and the rate constant ratios k_1/k_2 obtained from least-squares analyses are given in Table 1. These rate constant ratios k_1/k_2 are placed on an absolute basis using the recommended rate constants k_2 for the reference compounds[1] (see footnotes to Table 1), and are also included in Table 1.

These are the first reported rate constants for these reactions of 4,5-dihydro-2-methylfuran. These OH radical, NO_3 radical, and O_3 reaction rate constants are all high, comparable to what

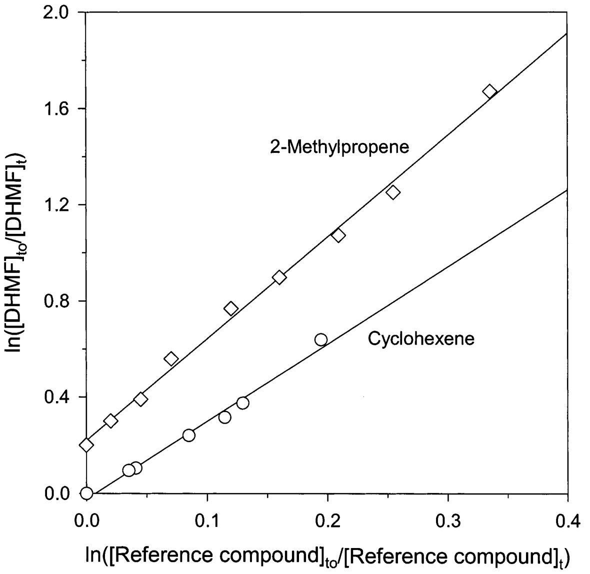


Figure 2. Plots of eq I for the reaction of OH radicals with 4,5-dihydro-2-methylfuran (DHMF), with cyclohexene and 2-methylpropene as the reference compounds. Note that for clarity the data with 2-methylpropene as the reference compound has been shifted vertically on the *y*-axis by 0.2 unit.

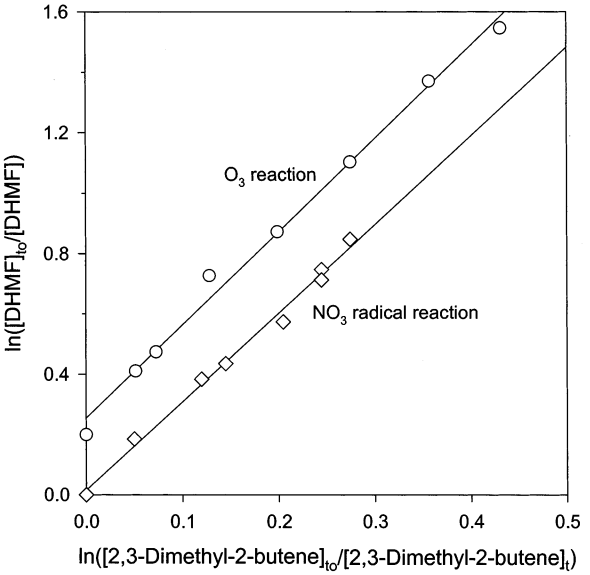


Figure 3. Plots of eq I for the reactions of NO_3 radicals and O_3 with 4,5-dihydro-2-methylfuran (DHMF), with 2,3-dimethyl-2-butene as the reference compound. Note that for clarity the data for the O_3 reaction has been shifted vertically on the *y*-axis by 0.2 unit.

may be expected for an alkene containing dialkyl and ether substituents, $R_2C{=}CHOR$,[25−28] and proceed mainly or solely by initial addition of OH radicals, NO_3 radicals, and O_3 to the C=C bond.[25−28] Grosjean and Grosjean[29] have reported a rate constant at 288 ± 1 K for the reaction of O_3 with ethyl 1-propenyl ether [$CH_3CH{=}CHOCH_2CH_3$] of $\geq(5.85 \pm 1.32) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}, reasonably consistent with the rate constant measured here for DHMF considering the additional substituent group attached to the C=C bond in DHMF. As shown in Table 1, the calculated lifetimes of DHMF are short during both daytime and nighttime.

Products of the DHMF Reactions. *Reaction with the OH Radical.* Spectra A and B of Figure 4 show the FT-IR spectra of products formed from DHMF during the irradiation of a $CH_3ONO{-}NO{-}DHMF{-}$air mixture, corresponding to 33% and 67%, respectively, of the initial 2.46×10^{14} molecules cm^{-3} DHMF being consumed by reaction. In Figure 4A,B, the absorption bands of the remaining DHMF and the products arising from CH_3ONO and NO (HCHO, HCOOH, CH_3ONO_2, HNO_3, HONO, $HOONO_2$, and NO_2) have been subtracted. The set of prominent bands at 1769, 1236, and 1057 cm^{-1} indicate the presence of an ester as a major product.[30a,31a] The C=O stretch region also shows the likely presence of an overlapped band at ∼1744 cm^{-1} which can be attributed to another carbonyl group. The relative intensities of the overlapped C=O stretch bands and the 1236 and 1057 cm^{-1} bands remained constant during the reaction, indicating that all of these absorption bands could belong to the same product. The major product expected from a consideration of the chemical mechanism involved (see

TABLE 1: Rate Constant Ratios k_1/k_2, Rate Constants k_1, and Estimated Lifetimes for the Reaction of 4,5-Dihydro-2-methylfuran with OH Radicals, NO_3 Radicals, and O_3 at 298 ± 1 K

reaction and reference compound	k_1/k_2[a]	k_1 (cm^3 molecule^{-1} s^{-1})[b]	lifetime[d]
OH radical reaction			
cyclohexene	3.22 ± 0.32	$(2.18 \pm 0.22) \times 10^{-10}$	
2-methylpropene	4.24 ± 0.22	$(2.17 \pm 0.12) \times 10^{-10}$	
		$(2.18 \pm 0.11) \times 10^{-10}$[c]	1.3 hr
NO_3 radical reaction			
2,3-dimethyl-2-butene	2.94 ± 0.20	$(1.68 \pm 0.12) \times 10^{-10}$	24 s
O_3 reaction			
2,3-dimethyl-2-butene	3.09 ± 0.21	$(3.49 \pm 0.24) \times 10^{-15}$	7 min

[a] Indicated errors are two least-squares standard deviations. [b] Placed on an absolute basis by use of rate constants k_2 for the reactions of OH radicals with cyclohexene and 2-methylpropene at 298 K of 6.77×10^{-11} cm^3 molecule^{-1} s^{-1} and 5.14×10^{-11} cm^3 molecule^{-1} s^{-1}, respectively;[1] a rate constant k_2 for the reaction of NO_3 radicals with 2,3-dimethyl-2-butene of 5.72×10^{-11} cm^3 molecule^{-1} s^{-1};[1] and a rate constant k_2 for the reaction of O_3 with 2,3-dimethyl-2-butene of 1.13×10^{-15} cm^3 molecule^{-1} s^{-1}.[1] The indicated errors in k_1 do not include the uncertainties in the values of k_2. [c] Weighted average. [d] Estimated on the basis of 24-hour average tropospheric concentrations (molecule cm^{-3}) of: OH radicals, 1.0×10^6;[42,43] NO_3 radicals, 2.5×10^8;[28] and O_3, 7.4×10^{11}.[44]

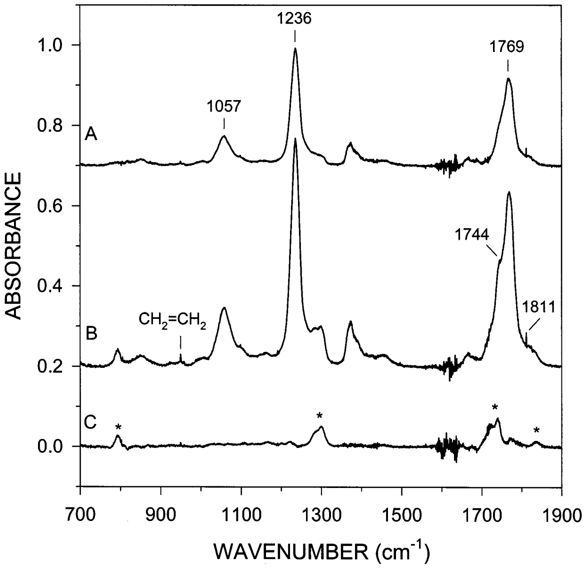
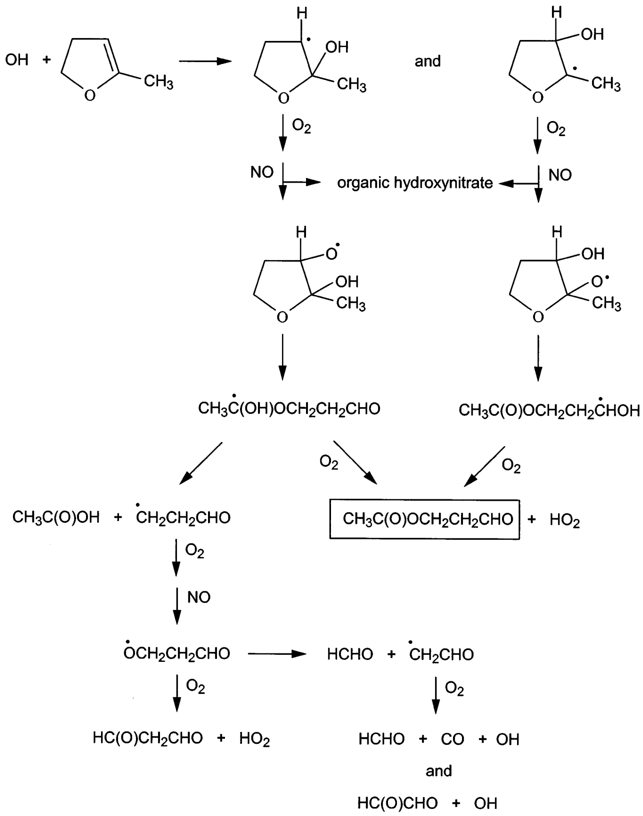


Figure 4. Infrared spectra of products attributed to DHMF from an irradiated $CH_3ONO{-}NO{-}DHMF{-}$air mixture corresponding to (A) 33% consumption and (B) 67% consumption of the initial 2.46×10^{14} molecules cm^{-3} DHMF (see text). (C) Residual spectrum resulting from a scaled subtraction of (A) from (B) to cancel the absorption bands of the major product $CH_3C(O)OCH_2CH_2CHO$. Asterisks denote absorption bands attributed to $RC(O)OONO_2$.

SCHEME 2



Scheme 2) and which is consistent with the infrared spectrum is $CH_3C(O)OCH_2CH_2CHO$ (molecular weight 116). The formation of increasing but minor amounts of $CH_2{=}CH_2$, as indicated by the Q-branch feature at 950 cm^{-1}, can also be seen in Figure 4.

A subtraction of the spectrum of Figure 4A, with the appropriate scale factor, from the spectrum of Figure 4B to cancel out the absorption bands of $CH_3C(O)OCH_2CH_2CHO$ resulted in Figure 4C, which shows absorption bands of a minor product(s) formed during the latter part of the reaction. The residual bands at approximately 1835, 1730, 1290, and 790 cm^{-1} (Figure 4C) are characteristic of acyl peroxynitrates, $RC(O)OONO_2$,[32] although minor amounts of alkyl peroxynitrates, $ROONO_2$, may also be contributing to the three lower frequency band positions. A possible product is $CH_3C(O)OCH_2CH_2C(O)OONO_2$, which is expected to be formed as a second-generation product from $CH_3C(O)OCH_2CH_2CHO$.[3,25]

FT-IR analysis of an irradiated $(CH_3)_2CHONO$−NO−DHMF−air mixture showed the formation of HCHO, with the measured yield increasing with the extent of reaction, being 5.4% after 1 min and 12% after 4 min of irradiation (corresponding to 13% and 59% consumption, respectively, of the initial 2.46×10^{14} molecules cm^{-3} DHMF). It was verified from a separate $(CH_3)_2CHONO$−NO−air irradiation, employing the same light intensity and initial concentrations as in the run with DHMF present, that the major product formed from $(CH_3)_2CHONO$ is acetone, with negligible formation of HCHO at irradiation times of 1 and 4 min. The increase of HCHO yield with irradiation time in the DHMF experiment is therefore attributed to HCHO formation from secondary reactions.

The results of GC−MS and API-MS analyses of irradiated CH_3ONO−NO−DHMF mixtures demonstrated the formation of a major product of molecular weight 116 from DHMF. GC−MS analyses of the *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine-coated SPME fiber exposed to the reaction products showed a large product peak whose mass spectrum had an $[M + H]^+$ base ion corresponding to the oxime of a molecular weight 116 carbonyl product at $[M + H]^+ = 312$ u. The mass spectrum also exhibited an intense fragment ion resulting from a loss of 60 ($CH_3C(O)OH$) from the molecular ion. The compound therefore contained a carbonyl group and an ester $CH_3C(O)O-$ group, consistent with this product being $CH_3C(O)OCH_2CH_2CHO$. It should be noted that the oxime of 5-hydroxy-2-pentanone was also observed in both the pre- and postreaction SPME analyses.

API-MS spectra of nonreacted CH_3ONO−NO−DHMF−air mixtures (in air at ~5% relative humidity) consist of ion peaks at 85, 169, 187, 205, and 253 u which are attributed to protonated DHMF, the protonated dimer, the monohydrated protonated dimer, dihydrated protonated dimer, and the protonated trimer, respectively. Note that the presence or absence of 5-hydroxy-2-pentanone cannot be discerned in the API-MS spectra, since ion peaks at 187 and 85 u are also expected from 5-hydroxy-2-pentanone. API-MS spectra of irradiated CH_3ONO−NO−DHMF−air mixtures showed, at total irradiation times of 10, 30, and 40 s, an additional ion at 201 u which API-MS/MS “fragment ion” spectra showed to be a protonated heterodimer of DHMF and a molecular weight 116 product. After longer irradiation times, product ion peaks due to additional products of molecular weight 86, 100, and 132 were observed. It is possible that these 86, 100, and 132 molecular weight products arise from secondary reactions and/or formation and reaction of 5-hydroxy-2-pentanone from the hydrolysis of DHMF in these experiments. Reaction of OH radicals with 5-hydroxy-2-pentanone is expected to proceed largely by H-atom abstraction from the C−H bonds of the CH_2 groups at the 4- and 5-positions,[26] leading in the presence of NO to the formation of $CH_3C(O)CH_2CHO$ (molecular weight 86) and $CH_3C(O)CH_2CH_2CHO$ (molecular weight 100), respectively.[1,25] Previous, preliminary, API-MS analyses of irradiated CH_3ONO−NO−5-hydroxy-2-pentanone−air mixtures (~5% relative humidity) in our laboratory showed the formation of products of molecular weights 100 and 86.[33]

While $CH_3C(O)OCH_2CH_2CHO$ was identified by GC−MS as its oxime, quantitative measurements could not be made by GC−MS because of the lack of an authentic standard. Quantification of $CH_3C(O)OCH_2CH_2CHO$ was therefore carried out using an average absorption coefficient obtained from the ~1240 cm^{-1} IR bands of $CH_3C(O)OCH_2CH_3$, $CH_3C(O)OCH_2CH_2{=}CH_2$, and $CH_3C(O)OCH_2Cl$, with an average peak-to-baseline absorption coefficient of $(7.89 \pm 0.50) \times 10^{-19}$ cm^2 molecule^{-1} and an average integrated (baseline-corrected) absorption coefficient of $(2.27 \pm 0.11) \times 10^{-17}$ cm molecule^{-1}. $CH_3C(O)OCH_2CH_2CHO$ concentrations derived from spectra such as those shown in Figure 4A,B using these two absorption coefficients agreed to within 5%, and the average value was adopted for each spectral record. These estimated $CH_3C(O)OCH_2CH_2CHO$ concentrations were then corrected for secondary reaction with the OH radical,[34] using the rate constant measured here for the reaction of OH radicals with DHMF and an estimated rate constant of 2.7×10^{-11} cm^3 molecule^{-1} s^{-1} for reaction of OH radicals with $CH_3C(O)OCH_2CH_2CHO$.[26] The corrections for secondary reaction were ≤8%. The formation yield of $CH_3C(O)OCH_2CH_2CHO$, determined from a least-squares analysis of a plot of the corrected $CH_3C(O)OCH_2CH_2CHO$ concentrations against the amounts of DHMF reacted, is given in Table 2 together with the range of observed yields for the minor products HCHO and ethene.

TABLE 2: Products Identified and Their Formation Yields from the Gas-Phase Reaction of OH Radicals with 4,5-Dihydro-2-methylfuran

	molar yield		
product	FT-IR	API-MS	GC−MS
$CH_3C(O)OCH_2CH_2CHO$	0.74 ± 0.19[a]	major product obsd of MW 116	carbonyl product of MW 116 obsd
HCHO	0.054−0.12[b]		
$CH_2{=}CH_2$	0.034−0.048[b]		
$CH_3C(O)OH$	<0.02		
$RC(O)OONO_2$	obsd, secondary product		

[a] Estimated using an average absorption coefficient from a series of organic esters (see text). [b] Increased in yield with extent of reaction.

As noted above, the magnitude of the rate constant measured for DHMF indicates that the reaction proceeds by initial addition of the OH radical at the C═C bond. Subsequent addition of O_2 to form a peroxy radical, followed by reaction of the peroxy radical with NO, leads to formation of an organic nitrate or an alkoxy radical plus NO_2.[3]

$$R\bullet + O_2 \rightarrow ROO\bullet \quad (3)$$

$$ROO\bullet + NO \rightarrow RONO_2 \quad (4a)$$

$$ROO\bullet + NO \rightarrow RO\bullet + NO_2 \quad (4b)$$

The alkoxy radicals can then react with O_2, decompose by C−C bond scission, or isomerize through (typically) a six-membered transition state.[1−3] A possible reaction sequence following initial OH radical addition to the double bond is given in Scheme 2 (in this scheme and those that follow, products that were observed are shown in boxes). The expected products are the molecular weight 163 organic nitrates, $CH_3C(O)OCH_2CH_2CHO$ (molecular weight 116), and possibly acetic acid plus coproduct ($HC(O)CH_2CHO$, HCHO, and/or glyoxal). However, acetic acid was not observed, with an upper limit to its formation yield of 2% being determined based on its well-isolated “Q-branch” at 642 cm^{-1}. The expected major product arising after H-atom abstraction from the C−H bonds at the 4- and 5-positions of DHMF (abstraction is expected to be minor given the magnitude of the rate constant) is the unsaturated dicarbonyl $HC(O)CH{=}C(CH_3)OCHO$, for which no evidence was seen in the API-MS analyses.

Thus, the main product observed in the GC−MS, API-MS, and FT-IR analyses is attributed to the molecular weight 116 aldehyde−ester $CH_3C(O)OCH_2CH_2CHO$. The appearance of the weak but distinct 1811 cm^{-1} absorption feature (Figure 4), which grew in proportion with the absorption bands of the ester during the reaction, indicates the formation of an additional minor primary product from DHMF. Although the sharp peak observed at 1811 cm^{-1} (Figure 4) is generally consistent with the C═O stretch of lactones,[30a,31c] the vapor-phase infrared spectrum of an authentic sample of α-angelicalactone (4-hydroxy-3-pentenoic acid γ-lactone), a potential product of the H-atom abstraction route, showed the corresponding Q-branch absorption to be at 1834 cm^{-1}. The estimated yield of $CH_3C(O)OCH_2CH_2CHO$ of 74 ± 19%, together with the expected formation of organic nitrates in small yield from the $RO_2^{\bullet}$ + NO reactions, accounts for most of the reaction products. Given the high reactivity of DHMF toward O_3, it is possible that some contribution of O_3 reaction to DHMF removal occurred in the experiments with FT-IR analyses, and this could account for the observation of small amounts of HCHO and ethene observed in the FT-IR analyses and possibly also of the molecular weight 132 product observed in the API-MS analyses at longer reaction times (see below).

Subsequent reaction of $CH_3C(O)OCH_2CH_2CHO$ with OH radicals will lead (in the presence of O_2) to the formation of the peroxyacyl radical $CH_3C(O)OCH_2CH_2C(O)OO\bullet$.[1,25] Reaction of $CH_3C(O)OCH_2CH_2C(O)OO\bullet$ with NO_2 will result in formation of the peroxyacyl nitrate $CH_3C(O)OCH_2CH_2C(O)OONO_2$,[25] which is presumably responsible for the acyl nitrate absorption bands observed in the FT-IR analyses.

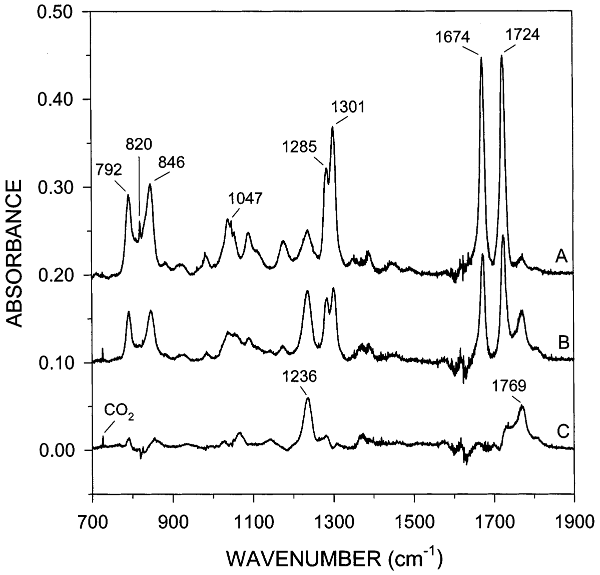


Figure 5. (A) Infrared spectrum of products attributed to DHMF from a reacted N_2O_5−NO_3−NO_2−DHMF−air mixture, corresponding to a 46% consumption of the initial 2.46 × 10^{14} molecules cm^{-3} DHMF after 3 min of mixing time (see text). (B) Infrared spectrum of the same mixture after 1 h. (C) Residual spectrum from a scaled subtraction of (A) from (B) to cancel the bands due to the product(s) $R(ONO_2)(OONO_2)$.

Reaction with the NO_3 Radical. Figure 5A shows an infrared spectrum of the major products from a mixture of 1.23 × 10^{14} molecules cm^{-3} N_2O_5 and 2.46 × 10^{14} molecules cm^{-3} DHMF after ∼3 min of mixing time, corresponding to 100% consumption of N_2O_5 and a 46% loss of DHMF. The absorption bands of the remaining DHMF and the other products NO_2, HNO_3, and HONO have been subtracted. Two sets of characteristic absorption bands are easily seen in Figure 5A: one set at 1674, 1285, and 846 cm^{-1} indicates the presence of an $-ONO_2$ group, and the second set at 1724, 1301, and 792 cm^{-1} is an absorption pattern attributed to an $-OONO_2$ group. The simultaneous presence of these two sets of bands suggests the formation of an $R(ONO_2)(OONO_2)$-type compound, an expected initial and thermally labile product.[1] A similar product spectrum obtained after the mixture was left for 1 h in the chamber is shown in Figure 5B, where a decrease in the intensity of the bands attributed to the $R(ONO_2)(OONO_2)$ product is seen along with the possible growth of absorption bands by other products. Figure 5C resulted from a scaled subtraction of the spectrum of Figure 5A from that of Figure 5B, revealing that one product which increased in concentration has the same characteristic absorption bands as the ester product $CH_3C(O)OCH_2CH_2CHO$

TABLE 3: Products Identified and Their Formation Yields from the Gas-Phase Reaction of NO_3 Radicals and O_3 with 4,5-Dihydro-2-methylfuran

	molar yield	
products	FT-IR	API-MS
NO_3 radical reaction		
$CH_3C(O)OCH_2CH_2CHO$	0.054−0.12[a]	
$R(ONO_2)(OONO_2)$	0.19−0.10[a]	
epoxide of MW 100	epoxide bands obsd	MW 100 product obsd
O_3 reaction		
$CH_3C(O)OCH_2CH_2CHO$	0.23 (0.22)[b]	MW 116 product obsd
HCHO	0.28 (0.36)[b]	
CH_3OH	0.095 (0.14)[b]	
HC(O)OH	0.021 (0.013)[b]	
$CH_2{=}C{=}O$	0.021 (0.020)[b]	
$CH_2{=}CH_2$	0.066 (0.076)[b]	
CO	0.20 (0.17)[b]	
CO_2	0.47 (0.51)[b]	
$CH_3C(O)OCH_2CH_3$	<0.03	

[a] Range of yields shown is for the analysis upon immediate consumption of N_2O_5 and the analysis obtained after the reaction mixture stood for 1 h (see text). [b] Values in parentheses were obtained in the absence of an OH radical scavenger.

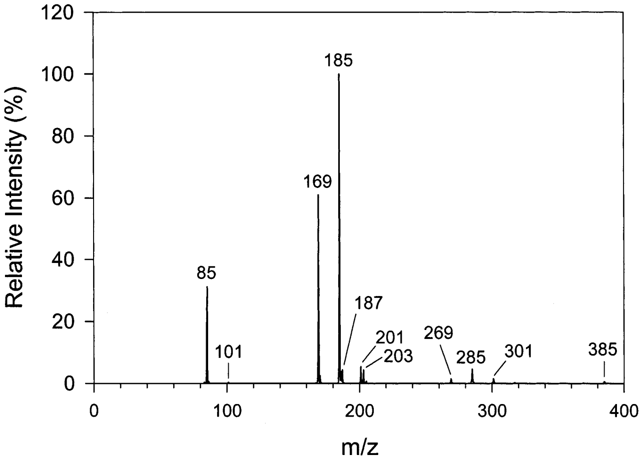


Figure 6. API-MS spectrum from a reacted N_2O_5−NO_3−NO_2−DHMF−air mixture.

formed during the reaction of DHMF with the OH radical (see Figure 4A). $CH_3C(O)OCH_2CH_2CHO$ concentrations were derived using the quantified spectra obtained from the OH + DHMF experiment, with the specific use of the isolated 1236 cm^{-1} band (Figure 5). The $R(ONO_2)(OONO_2)$ concentrations were estimated from the intensities of the 1674 cm^{-1} band, using the average integrated absorption coefficient of $(2.5 \pm 0.3) \times 10^{-17}$ cm $molecule^{-1}$ derived from corresponding absorption bands of a series of organic nitrates.[19] The ranges of yields obtained for $CH_3C(O)OCH_2CH_2CHO$ and $R(ONO_2)(OONO_2)$ are given in Table 3. Two weaker but distinct absorption features also appear in Figure 5A, at 1047 and 820 cm^{-1}, which are consistent with a C−O bond stretch and ring vibration of an epoxy group.[30b,31b] These absorptions decreased markedly with time (see Figure 5B), thus indicating that the possible epoxy compound formed in the DHMF + NO_3 reaction is thermally unstable. An authentic sample of the suspected epoxide product is not available.

An API-MS spectrum recorded from a reacted NO_3−N_2O_5−NO_2−DHMF−air mixture in the 7900 L Teflon chamber is shown in Figure 6. As noted above, the ion peaks at 85, 169, 187, and 203 u are attributed to protonated DHMF, the protonated dimer, and water adducts of the protonated dimer, and these were the only ion peaks present in the prereaction spectrum. API-MS/MS "product ion" spectra indicated that the ion peaks at 101, 185, 201, 269, 285, 301, and 385 u arising from reaction products were the protonated molecule and dimers of a product of molecular weight 100. The API-MS/MS "product ion" spectrum of the 201 u ion peak was significantly different from that of the 201 u ion peak observed in the OH radical initiated reaction and attributed to a protonated heterodimer of DHMF and $CH_3C(O)OCH_2CH_2CHO$. The API-MS analyses showed no significant evidence for the formation of a product of molecular weight 116, and no ion peaks were observed that correspond to the $R(ONO_2)(OONO_2)$ product(s) whose absorption bands dominated the FT-IR product spectra.

The expected reactions occurring during the reaction of NO_3 radicals with DHMF are shown in Scheme 3. The initial reaction involves addition of the NO_3 radical to the carbon−carbon double bond at the 2- and/or 3-positions, to form nitrooxyalkyl radicals which can decompose to the epoxide plus NO_2 (with this process typically decreasing in importance as the total pressure and O_2 content increases) or add O_2 to form nitrooxyalkyl peroxy radicals.[1,28] The nitrooxyalkyl peroxy radicals can react with NO_2 to form thermally unstable peroxynitrates

$$R(ONO_2)OO\bullet + NO_2 \leftrightarrow R(ONO_2)OONO_2$$

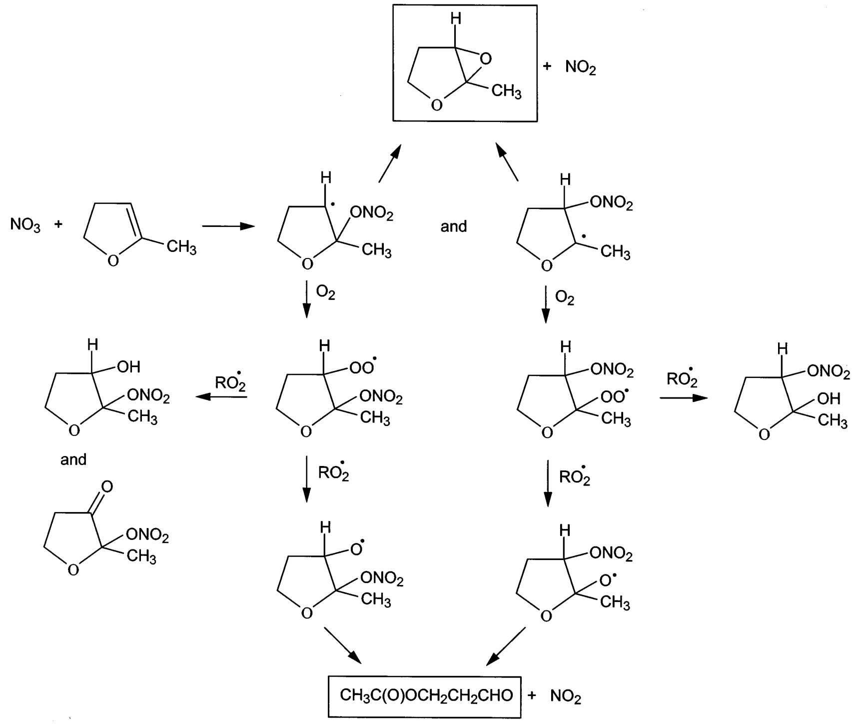
with HO_2 radicals to form nitrooxy hydroperoxides

$$R(ONO_2)OO\bullet + HO_2 \rightarrow R(ONO_2)OOH + O_2$$

and, as shown in Scheme 3, with organic peroxy ($RO_2^\bullet$) radicals. The reactions with organic peroxy radicals (including the self-reaction) proceed through a "molecular"channel, forming a nitrooxy alcohol and/or (if feasible) a nitrooxy carbonyl, and through a "radical" channel to form the nitrooxy alkoxy radical which, as shown in Scheme 3, is expected to decompose to form $CH_3C(O)OCH_2CH_2CHO$. Our FT-IR and API-MS analyses are consistent with Scheme 3, with formation of the molecular weight 100 epoxide and $CH_3C(O)OCH_2CH_2CHO$ (plus the thermally labile $R(ONO_2)OONO_2$ species) being observed and with nitrooxy alcohol, nitrooxy carbonyl, and nitrooxy hydroperoxide species accounting for the remainder of the products.

Reaction with O_3. The reaction of DHMF with O_3 occurred rapidly and was complete during the <3 min period of O_3 addition and mixing of the reactants. The FT-IR spectrum of the products from the reaction of 2.46×10^{14} molecules cm^{-3} DHMF with a total of 2.6×10^{14} molecules cm^{-3} O_3 (added in two equal aliquots) is presented in Figure 7A, where the absorption features of the low-molecular-weight products HCHO, CH_3OH, $CH_2{=}CH_2$, CO, and CO_2 are clearly seen. Subtraction of the absorptions by these compounds (except CO_2) from Figure 7A results in the spectrum of Figure 7B, which shows more clearly the presence of $CH_2{=}C{=}O$ (ketene) as a product, as well as the bands at 1769, 1236, and 1057 cm^{-1} assigned to $CH_3C(O)OCH_2CH_2CHO$, an expected major product. Subtraction of the absorption bands of $CH_3C(O)OCH_2CH_2CHO$ from Figure 7B using its IR spectrum derived from the OH radical reaction of DHMF (e.g., Figure 4A) resulted in Figure 7C, which shows distinct residual bands of unidentified products at 1283, 1725, and 1770 cm^{-1}. The comparison of $CH_3C(O)OCH_2CH_2CHO$ band intensities with those of the quantified spectra obtained from the OH radical experiment allowed the yields of $CH_3C(O)OCH_2CH_2CHO$ to be estimated. The same products were observed, with very similar yields

SCHEME 3



(defined as the amount of product formed/the amount of DHMF reacted), from an experiment conducted in the presence of sufficient cyclohexane to scavenge ≥90% of any OH radicals formed. The yields of the identified products from both experiments are listed in Table 3.

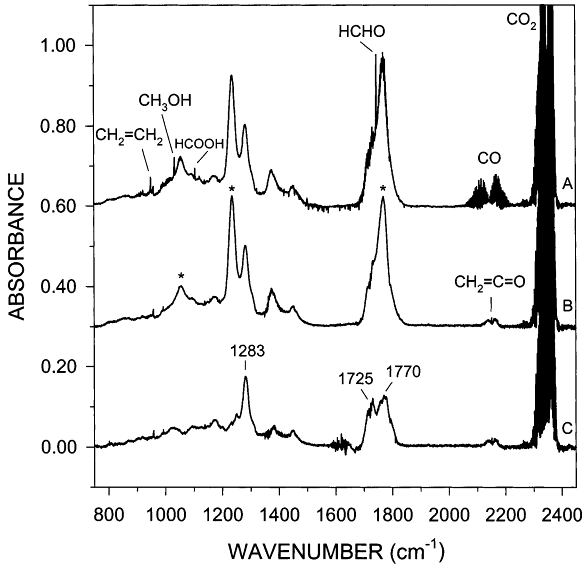


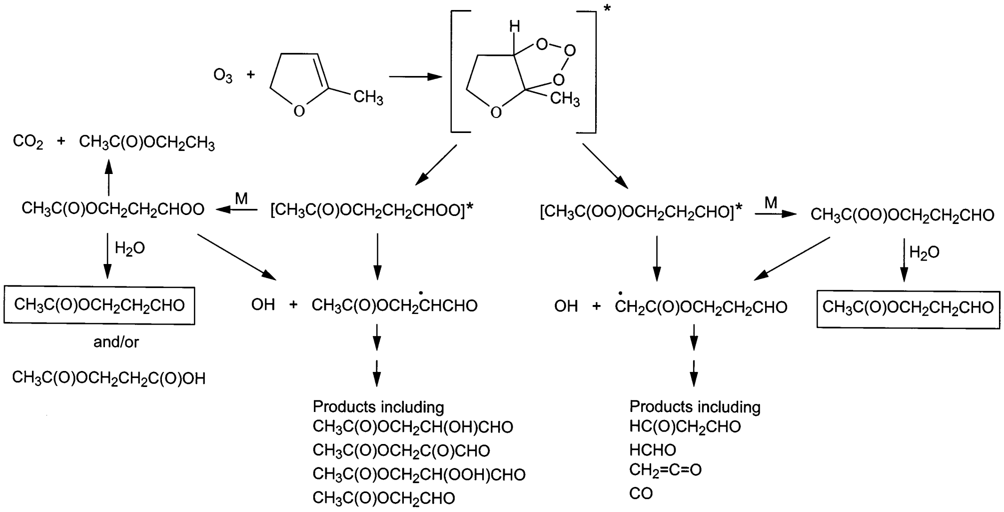
Figure 7. (A) Infrared spectrum of products from a reacted O_3−DHMF−air mixture. (B) Spectrum after subtraction of the absorption bands of HCHO, CH_3OH, CH_2═CH_2, and CO from (A). (C) Residual spectrum after subtraction of absorption bands (marked by asterisks in (B)) attributed to the product $CH_3C(O)OCH_2CHO$ (see text).

API-MS and API-MS/MS spectra of a reacted O_3−DHMF−cyclohexane−air mixture, with sufficient cyclohexane to scavenge >95% of any OH radicals formed, provided evidence for the formation of the same molecular weight 116 and 132 products observed in the OH radical initiated reaction (see above, noting that the molecular weight 132 product was observed in the OH radical initiated reaction at longer reaction times).

As shown in Scheme 4, the reaction of O_3 with DHMF involves initial addition of O_3 to the C═C bond to form an energy-rich primary ozonide, which rapidly decomposes to form two excited Criegee intermediates (theoretical calculations show these to be carbonyl oxides[35,36]). As shown in Scheme 4, these Criegee intermediates can decompose (through formation of a hydroperoxide) to an OH radical plus an organic radical coproduct, or be collisionally thermalized.[1] The $[CH_3C(OO)OCH_2CH_2CHO]^*$ intermediate is expected to primarily decompose to an OH radical plus $\bullet CH_2C(O)OCH_2CH_2CHO$ or be thermalized,[1] with the thermalized syn intermediate also decomposing to an OH radical plus $\bullet CH_2C(O)OCH_2CH_2CHO$.[37,38] The $[CH_3C(O)OCH_2CH_2CHOO]^*$ intermediate is expected to primarily decompose to an OH radical plus $CH_3C(O)OCH_2C\bullet HCHO$ (if in the syn configuration), decompose (through the "ester" channel) to CO_2 plus $CH_3C(O)OCH_2CH_3$, or be thermalized, with the thermalized syn intermediate also decomposing to an OH radical plus $CH_3C(O)OCH_2C\bullet HCHO$.[37,38] The thermalized intermediates can also react with water vapor to form $CH_3C(O)OCH_2CH_2CHO$ and/or $CH_3C(O)OCH_2CH_2C(O)OH$.[39−41]

The organic radical coproducts to the OH radical [$\bullet CH_2C(O)OCH_2CH_2CHO$ and $CH_3C(O)OCH_2C\bullet HCHO$] then react as do alkyl or substituted alkyl radicals in the absence of NO.[3] The products potentially formed from these $\bullet CH_2C(O)OCH_2CH_2CHO$ and $CH_3C(O)OCH_2C\bullet HCHO$ radicals[3] include the molecular weight 132 species $HOCH_2C(O)OCH_2CH_2CHO$ and $CH_3C(O)OCH_2CH(OH)CHO$, which may account for the molecular weight 132 product(s) observed in the API-MS analyses. Formation of CH_2═C═O may arise from decomposition of the $\bullet CH_2C(O)OCH_2CH_2CHO$ radical. Although the high yield of CO_2 (∼50%) could indicate that the ester channel is important in the decomposition of the $[CH_3C(O)OCH_2CH_2CHOO]^*$ intermediate, an upper limit to the formation yield of ethyl acetate of 3% was estimated from residual spectra such as that shown in Figure 7C. The similar yield of $CH_3C(O)OCH_2CH_2CHO$ (relative to DHMF reacted) in the presence and absence of the OH radical scavenger suggests that either the OH radical yield from the reaction of O_3 with DHMF is low or (more likely)

SCHEME 4



that the OH radical reaction with DHMF in the absence of NO_x also leads to formation of $CH_3C(O)OCH_2CH_2CHO$.

Atmospheric Implications. Our experiments and those of Cavalli et al.[14,23] show that 5-hydroxy-2-pentanone is converted to DHMF in dry diluent air or N_2, with a 5-hydroxy-2-pentanone lifetime of ~1.1 h in our chamber. Under dry conditions DHMF is not converted to 5-hydroxy-2-pentanone and DHMF is one of the most reactive volatile organic compounds studied to date with respect to reactions with OH and NO_3 radicals and O_3.[1,25,27,28] Based on 24-h average tropospheric concentrations (molecules cm^{-3}) of 1.0×10^6 for the OH radical,[42,43] 2.5×10^8 for the NO_3 radical,[28] and 7.2×10^{11} for O_3,[44] the calculated lifetimes for DHMF are 1.3 h for reaction with OH radicals (38 min for a 12-h average daytime OH radical concentration of 2.0×10^6 molecules cm^{-3}), 24 s for reaction with NO_3 radicals, and 7 min for reaction with O_3.

However, in moist air, DHMF converts to 5-hydroxy-2-pentanone (with a DHMF lifetime of ~3.5 h at 5% relative humidity in our chamber). The OH radical reaction rate constant for 5-hydroxy-2-pentanone estimated from the structure−reactivity relationship of Kwok and Atkinson[26] (as revised by Bethel et al.[45]) is 1.4×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, which corresponds to an estimated tropospheric lifetime of 0.8 day. Furthermore, 5-hydroxy-2-pentanone is not expected to react with O_3 and its reaction with NO_3 radicals is likely to be several orders of magnitude slower than that of DHMF. Therefore, in the atmosphere the reactive species (DHMF vs 5-hydroxy-2-pentanone) depends critically on the equilibrium ratio of DHMF and 5-hydroxy-2-pentanone resulting from their interconversion (Scheme 1) and may be different at nighttime than that at daytime. It is possible that in the lower troposphere the dominant species is 5-hydroxy-2-pentanone, although even a small fraction of DHMF could lead to removal of DHMF/5-hydroxy-2-pentanone through reaction of DHMF with OH radicals, NO_3 radicals, and/or O_3. Clearly, further work is needed to investigate the interconversion of these two species as a function of water vapor content and the effect of surfaces on the rates of interconversion should also be examined. Finally, the atmospheric behavior of larger 1,4-hydroxycarbonyls formed from alkane photooxidations, and of their corresponding dihydrofuran interconversion products, may well be similar to those of 5-hydroxy-2-pentanone and 4,5-dihydro-2-methylfuran.

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