

Atmospheric Photochemical Degradation of 1,4-Unsaturated Dicarbonyls

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Introduction

The elucidation of details of photochemical reaction mechanisms for the oxidation of aromatic volatile organic compounds remains a major problem (1). This is because there are apparently a large variety of photooxidation products formed in the reactions. Each of these products further reacts apparently in ways that are different from the better-understood alkane and simple alkene monofunctional products. The total reacted carbon balance is still poor in the aromatic systems, mostly because of lack of appropriate analytical methods for detecting the product mixtures of those photochemical reactions.

One of the most important types of products generated in the reaction of monocyclic aromatic hydrocarbons with the hydroxyl radical under tropospheric conditions is 1,4-unsaturated dicarbonyls (2-4). Formation of butenedial from toluene and o-xylene, 4-oxo-2-pentenal from toluene, o- and m-xylene, and 3-hexene-2, 5-dione from p-xylene and 1,2,4-trimethylbenzene have all been experimentally observed and are postulated as ring-cleavage carbonyl products during the OH-initiated atmospheric degradation of those aromatic hydrocarbons (2,5, 6). These species are expected to be very reactive after they are formed in the atmosphere, undergoing reactions with OH and O₃ as well as directly photolyzing (2-4,7). Thus,

they may act as important sources of free radicals, promote organic aerosols, and serve as precursors of carboxylic acids, hydroperoxides, and oxidants such as O₃, PAN and peroxydicarboxylic acids (8). Detailed studies of the fates of these highly reactive compounds, however, are lacking. A thorough investigation of atmospheric photooxidation of these reactive intermediates, which appear to be major secondary products, is required if we are to have predictive knowledge of the fates of their precursors and clearly understand photochemical reaction mechanisms for aromatics.

A few investigations of the atmospheric chemistry of unsaturated 1,4-dicarbonyls (3, 4, 7) have been reported. Using Fourier transform infrared (FTIR) absorption spectrometry, Tuazon et al. (4) investigated the photolysis of cis- and trans-3-hexene-2, 5-dione and reactions of these isomers with OH and O₃ at room temperature. Methylglyoxal and formaldehyde were found to be the major products of the reaction with O₃, but methylglyoxal was not detected as a product of the reaction of the 3-hexene-2, 5-dione with OH radicals. They also reported that the rate constants of the cis and trans isomers of 3-hexene-2, 5-dione were $(1.8 \pm 0.2) \times 10^{-18}$ and $(8.3 \pm 1.2) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reaction with O₃ at $298 \pm 2 \text{ K}$, and $(6.3 \pm 0.6) \times 10^{-11}$ and $(5.3 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reaction with OH. Another compound of this category, 3,4-dihydroxy-3-hexene-2, 5-dione, has recently been examined by Wiesen et al. (7) with long-path FTIR absorption spectroscopy. These authors argued that a hydrated vicinal polyketone, 3,3-dihydroxyhexane-2, 4, 5-trione, was probably the major product during the reaction of OH radicals with the above enediol form of acetylformoin. They also conducted a series of reactions of OH radicals in a 1080-L quartz-glass chamber with butenedial, 4-oxo-2-pentenal, 3-hexene-2,5-dione, among others (3), concluding that the reaction with OH radicals and photolysis are two major atmospheric sinks for these species. Rate constants of OH radical reactions (in unit of

$10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) are: cis-butenedial, 5.2 ± 0.1 , trans-butenedial, $\geq 2.41 \pm 0.79$, cis/trans 4-oxo-2-pentenal, 5.58 ± 0.21 , cis-3-hexene-2,5-dione, 6.9 ± 2.1 , and trans-3-hexene-2,5-dione, 4.0 ± 0.4 . Rate constants of these compounds with O_3 were estimated from structure reactivity. To the best of our knowledge, there is no experimental report on rate constants of O_3 with butenedial and 4-oxo-2-pentenal in the literature.

In this paper, we report a study in the UNC outdoor smog chamber of both OH- and ozone-initiated photooxidation of three unsaturated 1,4-dicarbonyl compounds: butenedial, 4-oxo-2-pentenal, and 3-hexene-2, 5-dione. Carbonyl products and intermediates produced from reactions of these compounds with OH radicals and O_3 were measured, as were time series of a few carbonyl products. Rate constants for O_3 consumption by these compounds were also determined. Carbonyl products were analyzed by the O- (2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) derivative method coupled with the gas chromatography (GC) /ion trap mass spectrometry (MS) separation and detection. This method has been successful in identifying multifunctional carbonyls in other studies (9, 10). In daytime outdoor experiments, we began with oxides of nitrogen and butenedial, or 4-oxo-2-pentenal, or 3-hexene-2, 5-dione in the chamber. In nighttime experiments, ozone was injected at a constant rate into each side of the chamber for the duration of the experiment. One side was filled with an initial amount of the compound to be studied and about 100-150 ppmV cyclohexane as the OH radical scavenger. The other side served as a reference for O_3 concentration.

By comparison with their corresponding standards, four categories of products are found in the OH and O_3 initiated reactions, namely, simple aldehydes, dicarbonyls, unsaturated carbonyls, and hydroxy carbonyls. Many of these carbonyls are on the EPA's hazardous air pollutants (HAPs) list or are known to be toxic. We also observed a few compounds whose

molecular weights were obtained by mass spectra, but whose identities could not unambiguously be determined because of lack of standards. Their possible structures are discussed in the text. Rate constants of these 1,4-unsaturated dicarbonyls with O₃ were measured. We propose photooxidation schemes for the three unsaturated 1,4-dicarbonyls.

Experimental Section

Carbonyl Reactants Preparation. Butenedial, 4-oxo-2-pentenal, and 3-hexene-2, 5-dione were synthesized by a collaborating organic chemist from commercially available compounds, such as furan, 2-methylfuran, and 2,5-dimethylfuran. Details of these synthesis were described elsewhere (11). The purity of these compounds as measured by NMR is greater than 90%.

Chamber Experiments. All experiments were carried out in the UNC 300,000-liter dual outdoor chamber located in Chatham County, North Carolina. As listed in Table 1, the daytime chamber experiments were conducted in the presence of NO_x, while the nighttime experiments were performed in the presence of O₃ and 100-150 ppmV cyclohexane. The latter was used as the OH radical scavenger. Cyclohexane can scavenge more than 90% of the OH radicals produced in the O₃-dicarbonyl reaction system. As gas phase internal standard 0.11 ppmV fluoroacetone, was also injected in each of these experiments. Detailed descriptions of the chambers, instruments employed, analytical methods and procedures used are available elsewhere (9,10,12). NO_x, O₃, and some hydrocarbons were monitored by instruments directly connected to the sample line of the chamber. Samples for the PFBHA derivative analysis were collected directly underneath the chamber through 0.5 m sampling lines to impingers containing 10 ml of 0.25 mg ml⁻¹ PFBHA-H₂O. The Saturn II GC ion trap MS used a 60 m x 0.32 mm x 0.50 μm DB-5 MS-grade, chemically-bonded, fused-silica capillary column (J & W Scientific).

Batch (integrated) samples were collected from the beginning to the end of the experiments, while time-series samples were taken at 30-minute intervals throughout experiment. Background concentrations of NO_x, O₃, and hydrocarbons were also measured.

Quantification. Identification and quantification of products were based upon commercially available or synthesized standards. If standards are not available, the relative concentration defined as the peak area ratio of the m/z 181-ion peak of a carbonyl to the m/z 181-ion peak of fluoroacetone was used to represent the response of the carbonyl compound.

Volatile carbonyls can easily be injected into the chamber and calibrated either by GCs directly connected to the sample line of the chamber or by the PFBHA derivatization method. For high boiling point polar compounds, e.g., hydroxyacetone, glyoxal, methylglyoxal, and glycolaldehyde, direct injection into the chamber is difficult. To solve this problem, we used a Collison nebulizer for injection. We assumed that after injected in the chamber the relative ratio of each compound in the solution remains the same as in the nebulizer solution. By using a nebulizer injection internal standard, the concentration of other compounds could be calculated according to the carbonyl's ratio and the known internal standard concentration. C₅-hydroxy carbonyls such as 4-OH-3-methyl-2-butanone and 3-OH-3-methyl-2-butanone were found to be appropriate standards. They are polar enough so that they will not be off-gassed when injected by nebulizer and yet, they have sufficiently low boiling points that they can be directly injected into the chamber.

Three sets of calibration curves were made for the PFBHA derivatization-GC ion trap MS measurement. One was for volatile carbonyl compounds. Their calibration curves were obtained from the PFBHA method and evaluated by comparing their quantification results with those from GCs connected to the chamber sample lines. The second set was for polar compounds

injected by nebulizer. The third set was for unstable compounds, such as glycidldehyde and malonaldehyde. The last set was made by aqueous standards corrected for collection efficiency and sample line loss. The slopes of these calibration curves, i.e. response factors, were used to calculate corresponding concentrations. The measurement precision in the entire workup procedure for the PFBHA measurement was estimated to be $\pm 20\%$. Time series of reactants and products were determined by these calibration curves.

Ozone Decay Measurement. Two chamber sides enable us to calculate the O_3 concentration consumed in the nighttime experiment. The second-order rate constants of O_3 with 1,4-unsaturated dicarbonyls were estimated by monitoring the rate of change of ozone decay in the presence of known concentrations of the dicarbonyls. The processes for removing ozone are



Hence,

$$d[O_3] / dt = (k_1 + k_2[\text{dicarbonyl}])[O_3]. \quad (3)$$

where k_1 and k_2 are the rate constants for Reactions (1) and (2). If $[\text{dicarbonyl}] \gg [O_3]_{\text{initial}}$, the ozone decay is given by

$$-d\ln[O_3] / dt = k_1 + k_2[\text{dicarbonyl}]. \quad (4)$$

A plot of the ozone decay rate against the dicarbonyl concentration should be a straight line with k_2 as the slope and k_1 the intercept.

In our experiment, the ozone was injected by alternating the O_3 generator constant output and constant flow rate between the two chamber sides at a 4-sec interval for the entire duration of experiments. The O_3 concentration consumed ($\Delta[O_3]$) in the reaction system from time t to time $t + \Delta t$, is computed from

$$\Delta[O_3] = \Delta[O_3]_{reaction} - \Delta[O_3]_{blank} \quad (5)$$

where $\Delta[O_3]_{reaction}$ and $\Delta[O_3]_{blank}$ are the O_3 concentration changes from time t to time $t + \Delta t$ in the reaction chamber (O_3 -in-dicarbonyl) and the blank chamber (O_3 -in-blank).

Results and Discussion

Products in OH initiated 1,4-Unsaturated Dicarbonyl Reactions. Chamber conditions, including air temperature, dew point temperature, Eppley total solar radiation (TSR) / Eppley ultraviolet radiation (UV), and concentration time series of NO_x and O_3 in experiments conducted on June 18, 1998 and July 2, 1998 are illustrated in Figures 1 and 2. The carbonyl compounds that were detected are illustrated in Figures 3 - 5.

Formaldehyde, acrolein, glycolaldehyde, glyoxal, and malonaldehyde in butenedial, formaldehyde, methyl vinyl ketone, glycolaldehyde, hydroxyacetone, glyoxal, methylglyoxal, and malonaldehyde in 4-oxo-2-pentenal, and formaldehyde, acetaldehyde, hydroxyacetone, and methylglyoxal in 3-hexene-2, 5-dione have been identified and confirmed by the matching retention time and mass spectra of their corresponding standards in the daytime experiments. A trace amount of acetaldehyde and acetone are usually detected in the distilled water blank as well as some glyoxal and methylglyoxal in the chamber background. Among these compounds identified, glyoxal in butenedial, methylglyoxal and glyoxal in 4-oxo-2-pentenal, and methylglyoxal in 3-hexene-2, 5-dione have previously been reported as the major carbonyl products (3). The new carbonyls we detected belong to categories of unsaturated carbonyls (acrolein, methyl vinyl ketone), hydroxyl carbonyls (glycolaldehyde and hydroxyacetone), and dicarbonyls (malonaldehyde).

Also shown in Figures 3-5 are compounds whose molecular weights have been determined by mass spectra but their identities have yet to be unambiguously determined

because of lack of standards. They include (M value stands for the PFBHA derivative molecular weight) M267, M281, M283, M297, M309, M311, M323, M325, M328, M476, M490, M492, M504, M506, and M520. The possible structures of these unidentified carbonyls with known molecular weight are listed in Table 2. By comparing the standards available, we know M267 is *not* isobutyraldehyde, butyraldehyde, methyl ethyl ketone, glycidaldehyde, methylglyoxal (mono-derivative), or malonaldehyde (mono-derivative). M297 is *not* 3-hydroxy-3-methyl-2-butanone, 4-hydroxy-3-methyl-2-butanone, and 5-hydroxy-2-pentanone. M490 is *not* 2,4-pentadione. M311 is *not* 4-hydroxy-4-methyl-2-pentanone. M281/M476 is *not* mono/di-derivative of biacetyl. M283 is *not* pyruvic acid and methylacetone. Among these compounds, some of their molecular weights are equal to that of triones or quadra-ones which may support the point that polyketone may be important products in the photooxidation of aromatics (2, 3).

Products in O₃ Initiated 1,4-Unsaturated Dicarbonyl Reactions. As an example, chamber conditions including air temperature, dew point temperature, and concentrations of O₃ in the experiment conducted on July 7, 1998 are illustrated in Figure 6. In the nighttime experiment, O₃ was injected into both sides of the dual chamber continuously, with only one side containing the unsaturated dicarbonyl reactant. By comparing the time series of O₃ in both sides of the chamber, the O₃ concentration consumed in the reaction from Eq. (5) can be calculated. Carbonyl products detected in the O₃ initiated nighttime chamber experiments using cyclohexane as the OH scavenger are summarized in Table 3. Glyoxal and formaldehyde in butenedial, glyoxal, methylglyoxal, and malonaldehyde in 4-oxo-2-pentenal, and methylglyoxal in 3-hexene-2,5-dione were found as the major products in these systems. Also observed in these experiments were some carbonyls with known molecular weights but not one of the standards available. In addition we detected cyclohexanone, which is the product of OH with the added cyclohexane.

This shows that these unsaturated dicarbonyls do produce OH radicals, probably from Criegee biradical decomposition.

Time-series of Products. The products formed during the reaction in the UNC outdoor smog chamber can continue to undergo further photochemical processes. It is difficult to establish a mass balance for the photooxidation process of the unsaturated dicarbonyls studied in this paper. When a standard was available, a time series of a carbonyl is represented by its absolute concentration in a sample, otherwise, by its relative concentration. The latter data are still useful, especially when the time series of several related compounds are plotted together. One can observe how reactants decay, intermediates are first produced and then consumed, and how final products are eventually formed. Figures 7-11 present time series data of carbonyls in 4-oxo-2-pentenal and 3-hexene-2,5-dione daytime experiments. Figures 12-13 are time series of carbonyls in the nighttime experiment of 4-oxo-2-pentenal with O₃ and cyclohexane.

Plotted in Figure 7 are the daytime series of 4-oxo-2-pentenal, glyoxal, methylglyoxal, and malonaldehyde. As 4-oxo-2-pentenal is consumed rapidly in the early morning, glyoxal, methylglyoxal, and malonaldehyde are quickly produced, indicating that these three carbonyls are probably primary products. After they reach maxima at about 0900 EDT, these products themselves promptly decay to the secondary products, via either reactions with radicals in the chamber or by photolysis. Because 4-oxo-2-pentenal is nearly totally consumed by 1000 EDT the primary products maintain a low concentration throughout after 1000 EDT. Methylglyoxal, glyoxal, and malonaldehyde share the same pattern of formation and decay in Figure 7. While this suggests that methylglyoxal and glyoxal share a similar formation pathway, we have been unable to propose a formation mechanism for malonaldehyde from OH-attack followed by O₂ addition and NO-NO₂ conversion. More discussion of malonaldehyde formation follows later.

Shown in Figure 12 are the nighttime time series for the same compounds. Though this plot still shows that glyoxal, methylglyoxal, and malonaldehyde are primary products, the difference is obvious. As 4-oxo-2-pentenal slowly decays, the carbonyl products continuously build up. Figure 12 of course does not show the loss of these compounds due to photolysis (and, because OH is expected to be low in the Figure 12 nighttime condition, does not show significant loss by OH attack either). The time series also help us identify different unknown isomers. As shown in Figure 11 and 13, different chromatogram peaks showed the same molecular weight and almost had the same time series patterns implying that they are either one carbonyl compound or structurally similar isomers.

Ozone Reaction Rate Constants. Based on the method established in Eqs. (1)-(5), a least-squares analysis was used to determine the rate constants for O₃ reactions with butenedial, 4-oxo-2-pentenal, and 3-hexene-2,5-dione to be 1.6 ± 0.1 at 294-298 K, 4.8 ± 0.8 at 293-297 K, and 3.6 ± 0.3 (units in $10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) at 295-297 K (see Table 4). The indicated errors are two least-squares standard deviations of the slopes of the fitted line combined with an estimated overall uncertainty of $\pm 20\%$ in the PFBHA method. The carbonyls used in this study are mixtures of cis- and trans-1,4-unsaturated dicarbonyls. Our rate constant of O₃-3-hexene-2,5-dione is in reasonable agreement with the literature (4). This is the first experimental determination of k_{O_3} for butenedial and 4-oxo-2-pentenal, although estimation by the structure-reactivity method is available in the literature (3). The reaction of 1,4-unsaturated dicarbonyls with O₃ involves electrophilic addition of O₃ to the double bond and the reactivity correlates positively with the electronic density at the carbon-carbon double bond (13). Since the -CH₃ group is an electron donor, the anticipated reactivity order should be butenedial < 4-oxo-2-pentenal < 3-hexene-2,5-dione. Our results shows that 4-oxo-2-pentenal is most reactive and

butenedial is the slowest. This may imply that other species in the system are involved in the consumption of O_3 , and thus our model in Equations (1) to (5) may overestimate the rate constant of 4-oxo-2-pentenal.

1,4-Unsaturated Dicarbonyls Photooxidation Mechanisms. Based on these results, we can propose the photooxidation mechanisms of 1,4-unsaturated dicarbonyls shown in Schemes I and II. Compounds with bold M values and names were carbonyls identified in experiments. There are three major pathways available for 1,4-unsaturated to degrade: reaction with OH, reaction with O_3 , and photolysis. OH radicals can add to the double bond of the unsaturated dicarbonyls, generating hydroxy alkyl radicals. These radicals become hydroxy alkoxy radicals via reaction with O_2 , followed by NO- NO_2 conversion. Hydroxy alkoxy radicals can either undergo decomposition or react with O_2 via H-abstraction to generate various products. In butenedial and 4-oxo-2-pentenal, the OH radical can also abstract a H-atom from the -CHO group leading to the formation of unsaturated peroxy acyl radicals after reactions with O_2 . These peroxy acyl radicals can either convert NO to NO_2 or react with NO_2 to form unsaturated peroxyacyl nitrate compounds that are expected to be temperature labile.

As seen in the Scheme I and the time series data (Figure 7), glyoxal and methylglyoxal are major primary products from these reactions. After they are formed, they quickly undergo degradation to form secondary products such as formaldehyde, acetaldehyde, CO, peroxyacetyl nitrate (PAN), and peroxyacyl nitrates, etc.

We observed compounds with a derivative molecular weight of 476. Their possible structures are C_4 dicarbonyls and/or C_3 triones. Because they have similar time series patterns (Figures 8 and 11), they may be the PFBHA derivative isomers from the same carbonyl or structurally similar carbonyl isomers. These compounds could be formed as secondary products

from alkoxy radical decomposition in 4-oxo-2-pentenal-OH reaction. But our result shows that M476s are formed as early as glyoxal and methylglyoxal and then decreased quickly, suggesting that they are primary products as well. M476s have also been detected as primary products in the OH initiated 3-hexene-2, 5-dione reaction.

In the 4-oxo-2-pentenal reaction we observed an M283 compound whose possible structure is a C₄ hydroxy carbonyl, pyruvic acid, methyloxacetone, or C₃ hydroxy dicarbonyl. By comparing its retention time and mass spectra with standards, the possibilities of pyruvic acid and methyloxacetone were excluded. From Figure 8, it appears that it is a secondary product. Thus, the primary product C₄ hydroxy carbonyl which formed from alkoxy radical decomposition at 1,2 position could also be excluded. This suggests that alkoxy radical decomposition mainly occurred at 2,3 (3,2) position.

It has been reported that 1,4-unsaturated dicarbonyl photolysis is a strong sink in the atmosphere leading to the production of maleic anhydride, 3H-furan-2-one, 5-methyl-3H-furan-2-one (3). According to these investigators, an OH radical concentration of (3-4) x10⁷ molecules cm⁻³ would be required for the OH radical reaction to compete with photolysis loss of these dicarbonyls (14). Our PFBHA derivative method is unable to detect these anhydrides. Only a very small amount of methyl vinyl ketone was detected in 4-oxo-2-pentenal and of acrolein in butenedial. The time series of acrolein measured by us in the butenedial system (*not shown here, but in ref. 11*) shows that acrolein was formed earlier than glyoxal. This demonstrates that butenedial does photolyze quickly. We did not observe, however, the formation of 4-oxo-2-pentenal in the oxidation of 3-hexene-2, 5-dione that was reported in Ref. (2).

We identified glycolaldehyde in the butenedial-OH reaction and hydroxyacetone in OH-initiated 3-hexene-2, 5-dione. According to their time series, they are secondary products. One possible pathway for glycolaldehyde formation is via acrolein reacting with OH radicals.

A Varian 3700 GC- ECD (electron capture detector) is directly connected to the chamber sample lines and is used to detect PAN and N-containing compounds. PAN was detected in OH-initiated 4-oxo-2-pentenal and 3-hexene-2, 5-dione reactions. It was formed at about 1100 –1200 EDT and could be produced from products of dicarbonyls such as acetaldehyde and methylglyoxal. Comparing PAN's measurement with the N-containing compounds measured by the NO_x analyzer, which responds to virtually all RONO₂ and ROONO₂ compounds (Figure 9), we can see that within the measurement variation, the concentration of N-containing compounds measured later in the experiment on the NO_x analyzer is equal to the concentration of PAN formed in 4-oxo-2-pentenal/NO_x experiment. Note that during 0730–1100 EDT there was a huge gap between the NO_x analyzer measurement of N-containing compounds and GC-ECD measurement of PAN. During this period, NO₂ should be close to zero, because the shape of O₃ time series is flat. Only about 0.35 ppm 4-oxo-2-pentenal remained in the system during this time. Right after all the 4-oxo-2-pentenal was consumed, at about 1100-1200 EDT, O₃ started to build up again, and PAN began to get to its highest peak. This implies that some other unstable organic nitrate(s) formed during 0730 – 1100 EDT in this system. Most likely these compounds were unsaturated peroxyacyl nitrates, which formed from unsaturated peroxy acyl radicals reacting with NO₂. They apparently had a short lifetime as the temperature was increasing during this period, thus served as a temporary storage reservoir for NO_x. In contrast, Figure 5 of supporting data shows that in the 3-hexene-2, 5-dione experiments, PAN was not the only species detected by NO_x-analyzer after the parent hydrocarbon had been consumed.

Malonaldehyde as primary product was both found in OH initiated butenedial and 4-oxo-2-pentenal reactions. Unlike methylglyoxal and glyoxal, the formation of malonaldehyde can not be explained via rearrangement of the alkoxy radical formed after O₂ addition and NO to NO₂ oxidation. Rather an H-shift step appears necessary to produce this compound. After OH addition, such an H-shift followed by decomposition could result in the subsequent formation of malonaldehyde. For further details see ref. 11. Formation of this compound may share the same pathway as some of the unidentified compounds such as the M476 and M283 species.

It has been argued (4) that methylglyoxal was not a major product in the OH-initiated 3-hexene-2, 5-dione reaction. Instead, isomerization was claimed to be more important than decomposition. Our results do not confirm this argument as we did not detect the compounds that would result from isomerization, such as C₆ hydroxy triones. Our data strongly support that the reactions leading to methylglyoxal predominate.

Since O₃ was formed soon after sunrise in OH-initiated experiments, 1,4-unsaturated dicarbonyls also reacted with O₃ to yield the energy-rich ozonide during the daytime experiments. In nighttime reactions, however, with the use of high concentration cyclohexane as the OH radical scavenger, reaction with O₃ is the major pathway. Reaction pathways of 1,4-unsaturated dicarbonyls with O₃ are outlined in Scheme II. The energy-rich ozonide rapidly decomposes to methylglyoxal /glyoxal and an energy-rich biradical or forms epoxy carbonyls. The energy-rich biradicals can undergo stabilization and then react with H₂O to form organic acids or carbonyls. They can also decompose to produce carbonyls, OH radicals, and other products.

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Supporting Information Available

More figures from this study are available. They include chamber conditions and O₃ time series in O₃-dicarbonyls-cyclohexane experiments, time series of carbonyls in butenedial-NO_x experiment, time series of products in 3-hexene-2, 5-dione daytime and night experiments, O₃-dicarbonyl reaction rate constants, UV spectra of dicarbonyls. Also included are documents of synthesizing 1,4-undaturated dicarbonyls and figures of their NMR, MS spectra.

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Figure 1. Daytime dual smog chamber experiments on June 18, 1998. 1.5 ppmV 4-oxo-2-pentenal and 1.0 ppmV butenedial, and 0.60ppm nitrogen oxides. Top: NO, NO₂+RONO₂+ ROONO₂ and O₃ time series (NO₂+RONO₂+ ROONO₂ measured by NO_x analyzer). Bottom: Temperature-chamber air temperature, DewPoint-chamber dew point temperature, TSR-Eppley total solar radiation, UV-Eppley ultraviolet radiation.

Figure 2. Daytime dual smog chamber experiments on July 2, 1998. 0.9 ppmV 4-oxo-2-pentenal and 3-hexene-2, 5-dione, and 0.60ppm nitrogen oxides. Top: NO, NO₂+RONO₂+ ROONO₂ and O₃ time series (NO₂+RONO₂+ ROONO₂ measured by NO_x analyzer). Bottom: Temperature-chamber air temperature, DewPoint-chamber dew point temperature, TSR-Eppley total solar radiation, UV-Eppley ultraviolet radiation

Figure 3. Reconstructed m/z 181 ion chromatograph of the batch sample collected from a butenedial/NO_x outdoor smog chamber experiment in the daytime. Y-axis: Relative ion current of m/z 181 ion; X-axis: Retention time in min.

Figure 4. Reconstructed m/z 181 ion chromatograph of the batch sample collected from a 4-oxo-2-pentenal/NO_x outdoor smog chamber experiment in the daytime. Y-axis: Relative ion current of m/z 181 ion; X-axis: Retention time in min.

Figure 5. Reconstructed m/z 181 ion chromatograph of the batch sample collected from a 3-hexene-2,5-dione/NO_x outdoor smog chamber experiment in the daytime. Y-axis: Relative ion current of m/z 181 ion; X-axis: Retention time in min.

Figure 6. Nighttime dual smog chamber experiments on July 7, 1998. 0.9 ppmV 4-oxo-2-pentenal. O₃ and 150 ppmV cyclohexane. Top: O₃ time series. Bottom: Temperature-chamber air temperature, DewPoint-chamber dew point temperature.

Figure 7. Time series of glyoxal, methylglyoxal, malonaldehyde in the 4-oxo-2-pentenal daytime outdoor smog chamber experiment. R: right axis; L: left axis.

Figure 8. Time series of M283, M467 in the 4-oxo-2-pentenal daytime outdoor smog chamber experiment. R: right axis; L: left axis.

Figure 9. Time series of O₃, PAN and N-Containing compounds in the 4-oxo-2-pentenal daytime outdoor smog chamber experiment. R: right axis; L: left axis.

Figure 10. Time series of methylglyoxal, acetaldehyde, hydroxyacetone in the 3-hexene-2,5-dione daytime outdoor smog chamber experiment. R: right axis; L: left axis.

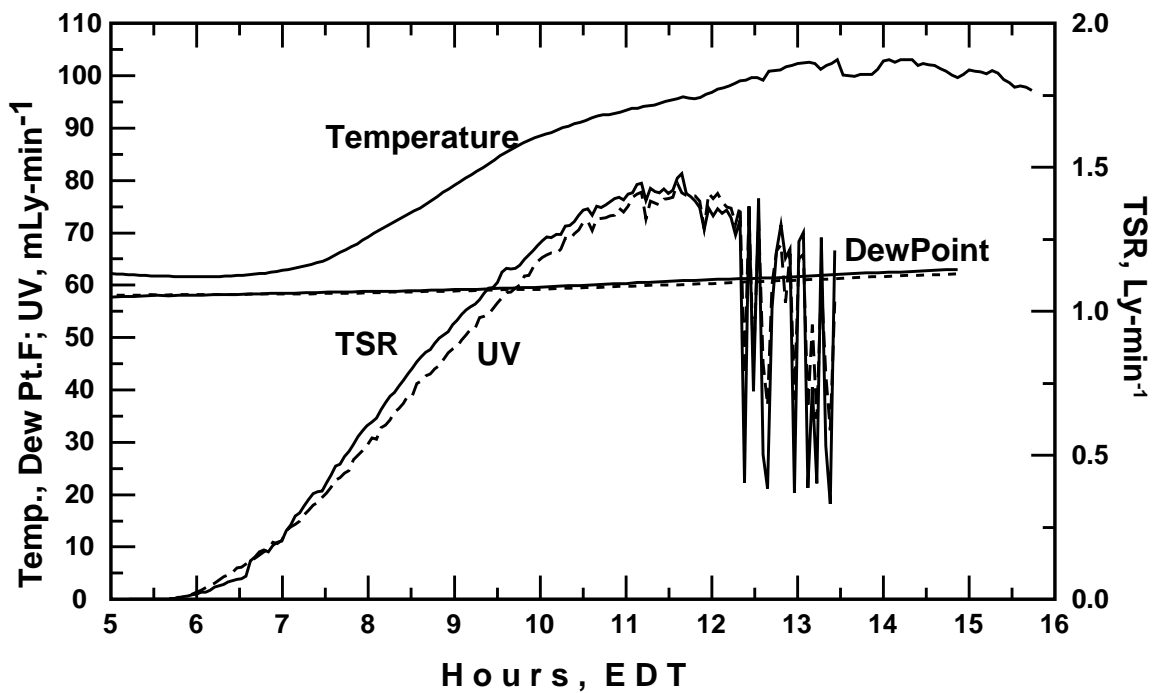
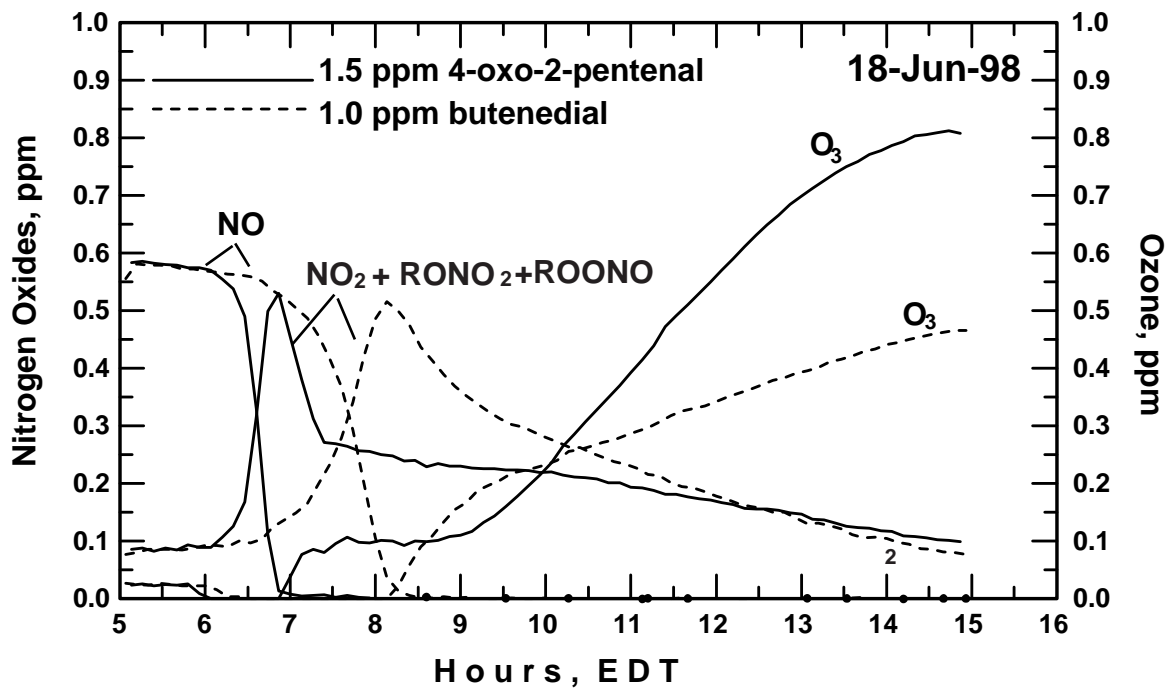
Figure 11. Time series of M267, M476 in the 3-hexene-2,5-dione daytime outdoor smog chamber experiment. R: right axis; L: left axis.

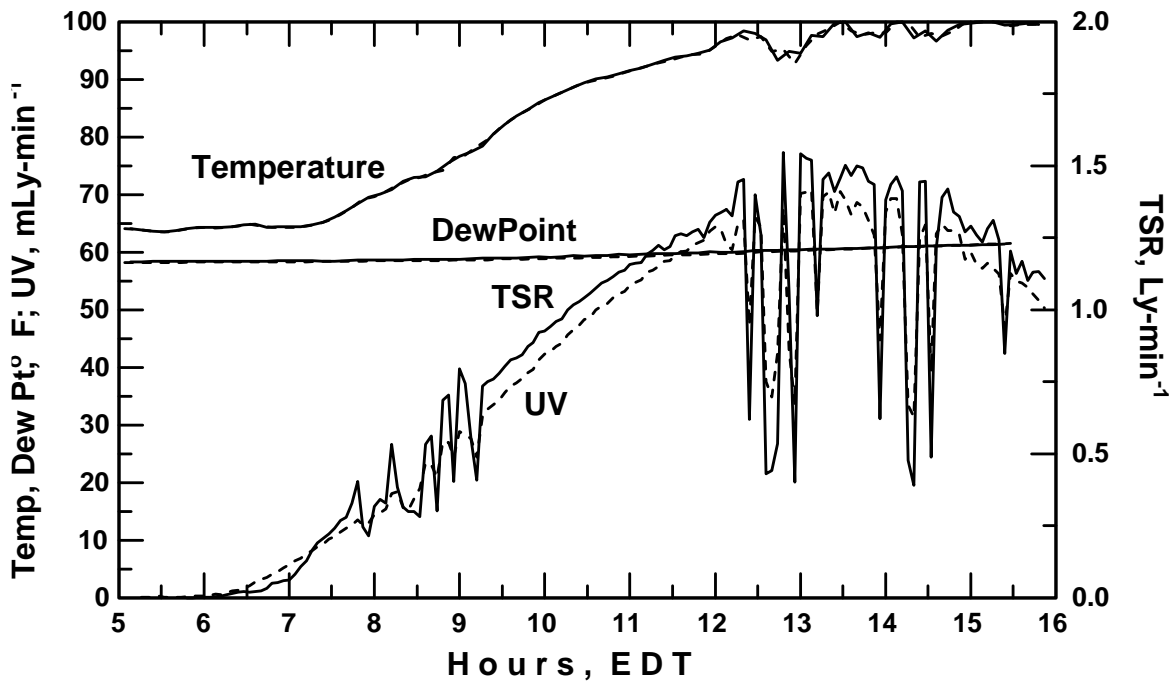
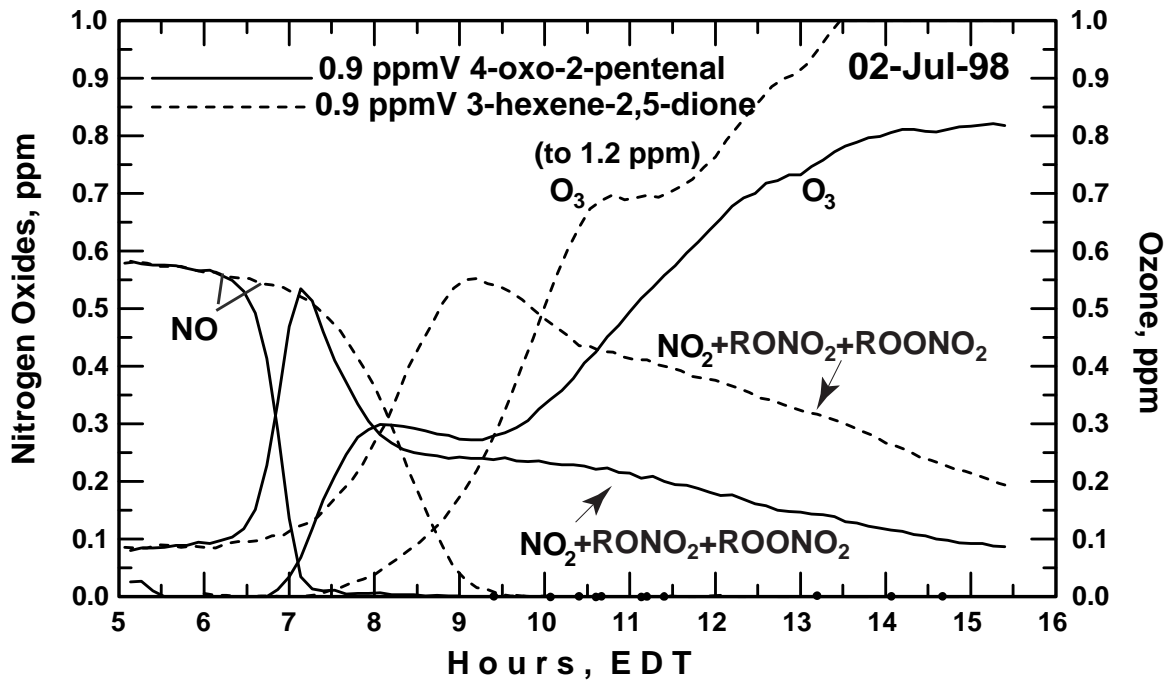
Figure 12. Time series of glyoxal, methylglyoxal, malonaldehyde in the 4-oxo-2-pentenal nighttime outdoor smog chamber experiment. R: right axis; L: left axis.

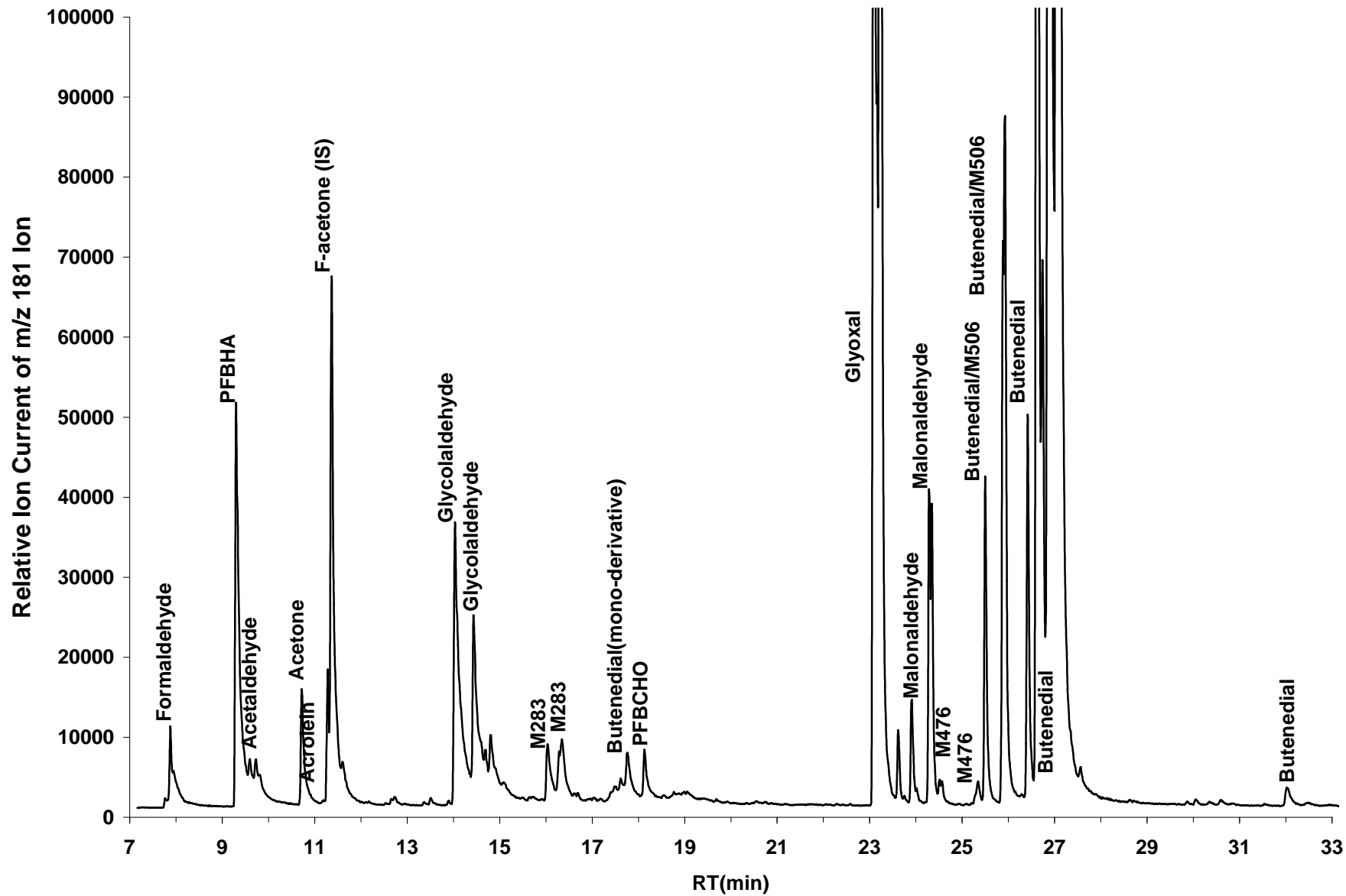
Figure 13. Time series of M476 in the 4-oxo-2-pentenal nighttime outdoor smog chamber experiment. R: right axis; L: left axis.

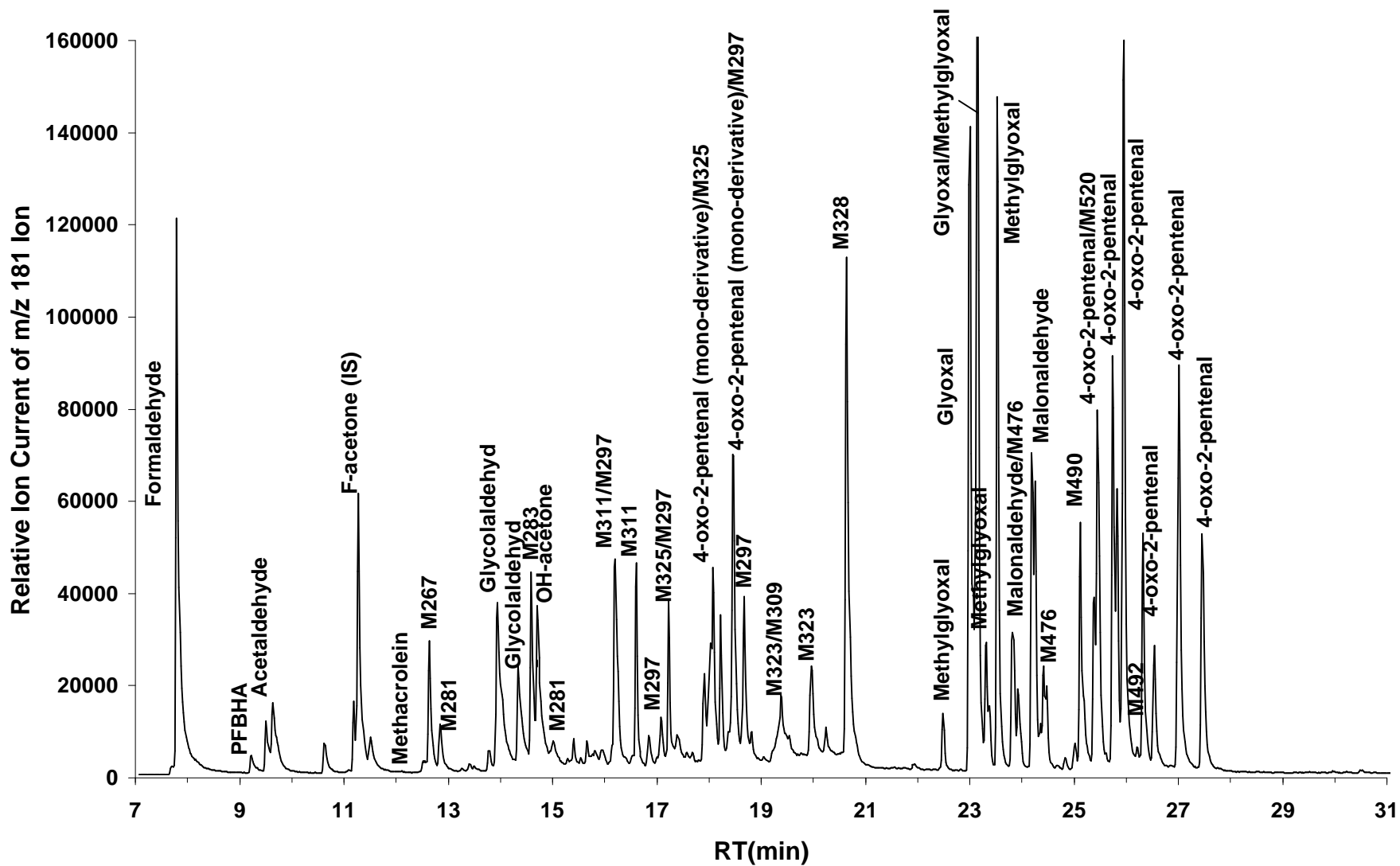
Secheme I. Photochemical degradation mechanisms of 1,4-unsaturated dicarbonyls with OH radicals and photolysis (**M** value and names represent products observed in the experiments).

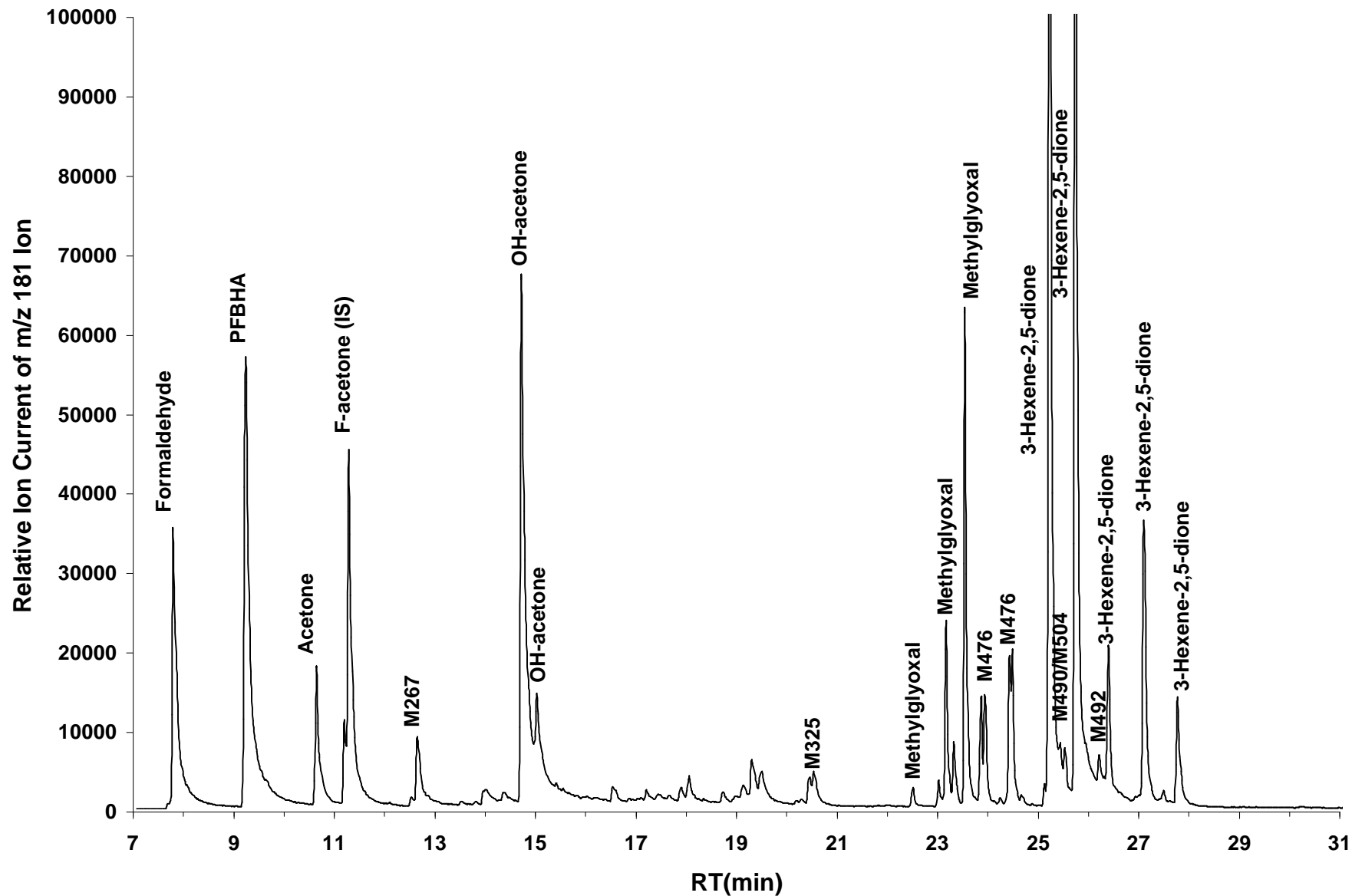
Secheme II. Photochemical degradation mechanisms of 1,4-unsaturated dicarbonyls with O₃ (**M** value and names represent products observed in the experiments).

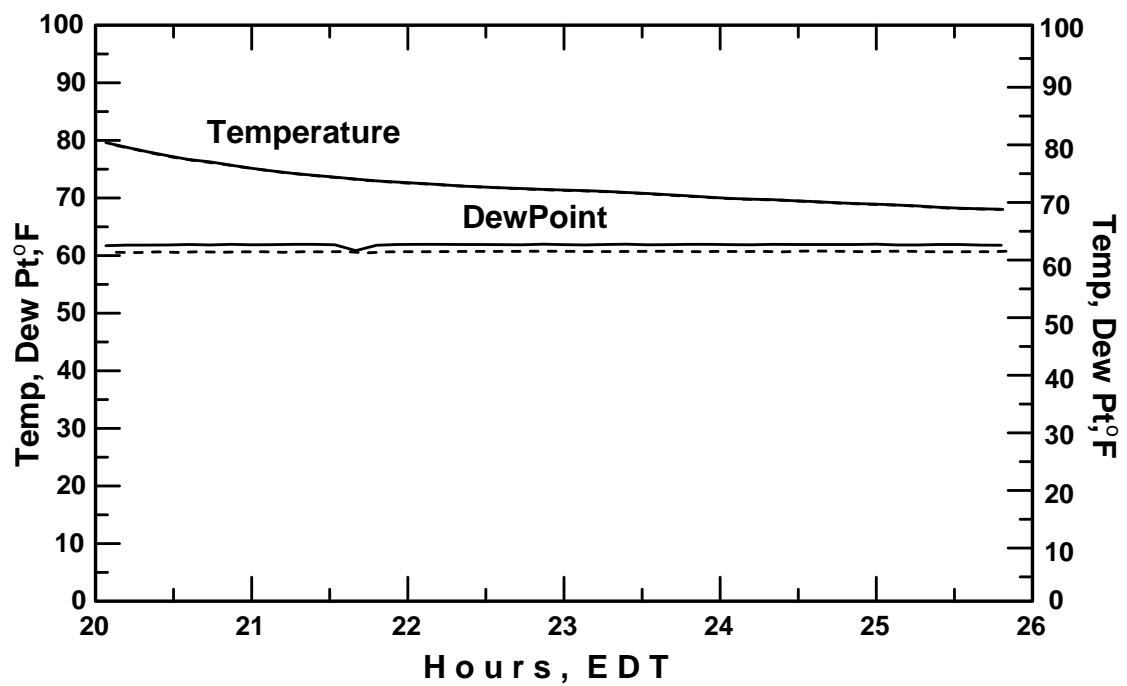
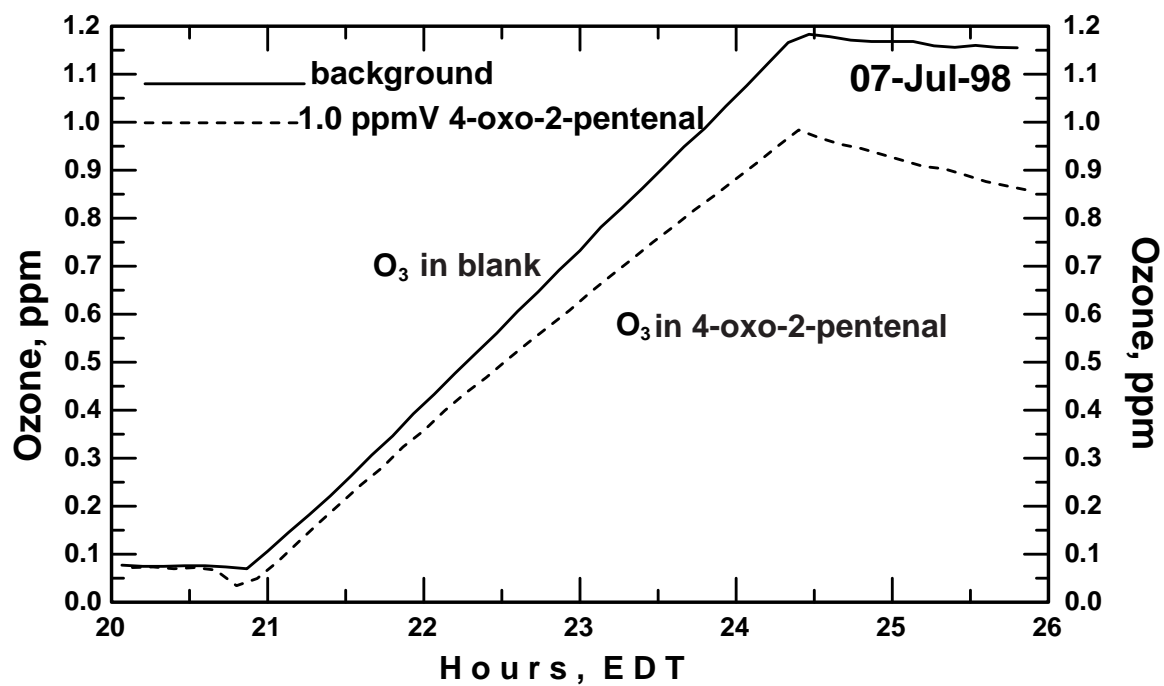


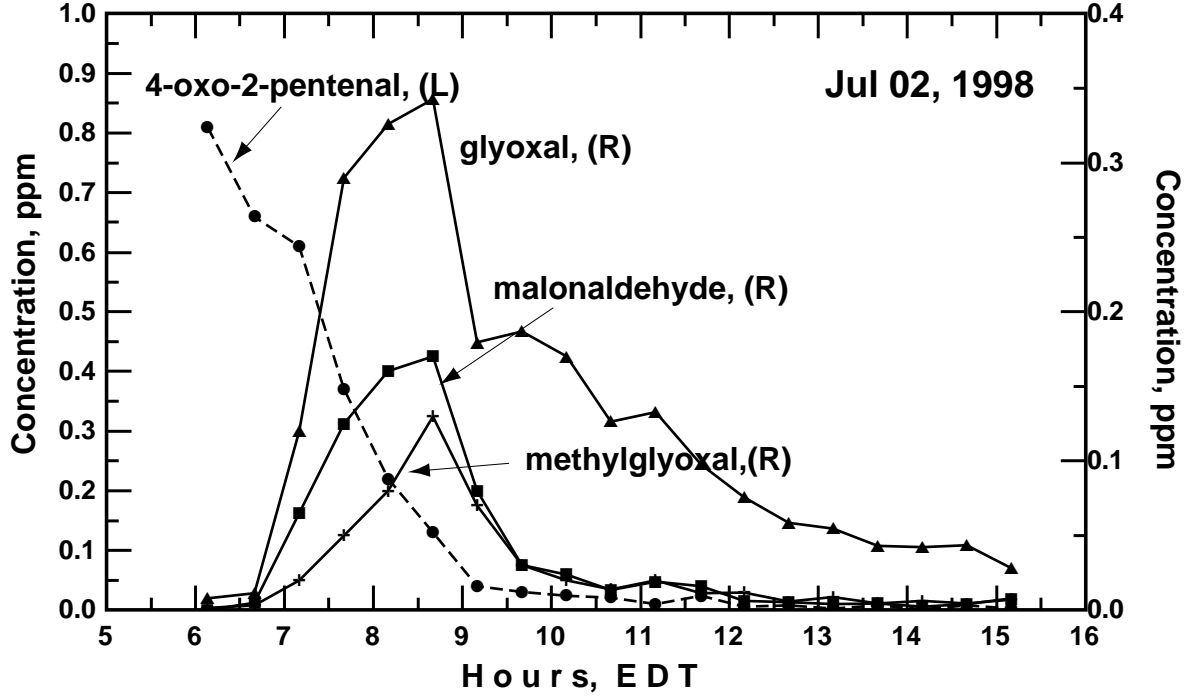


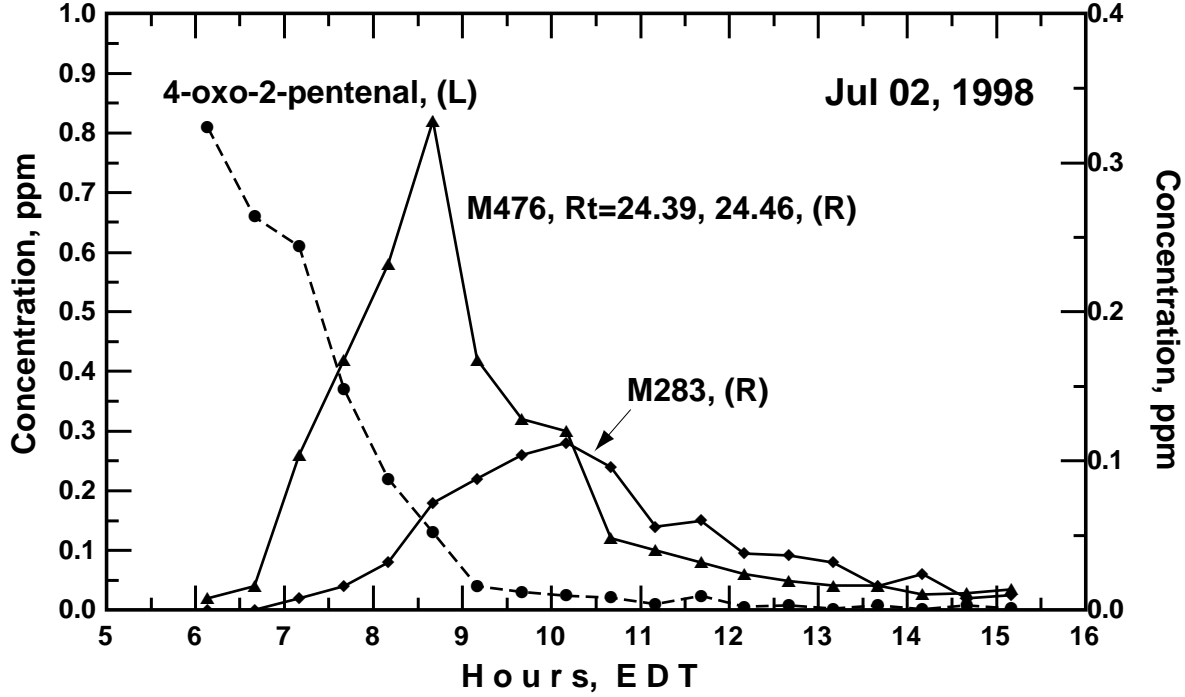


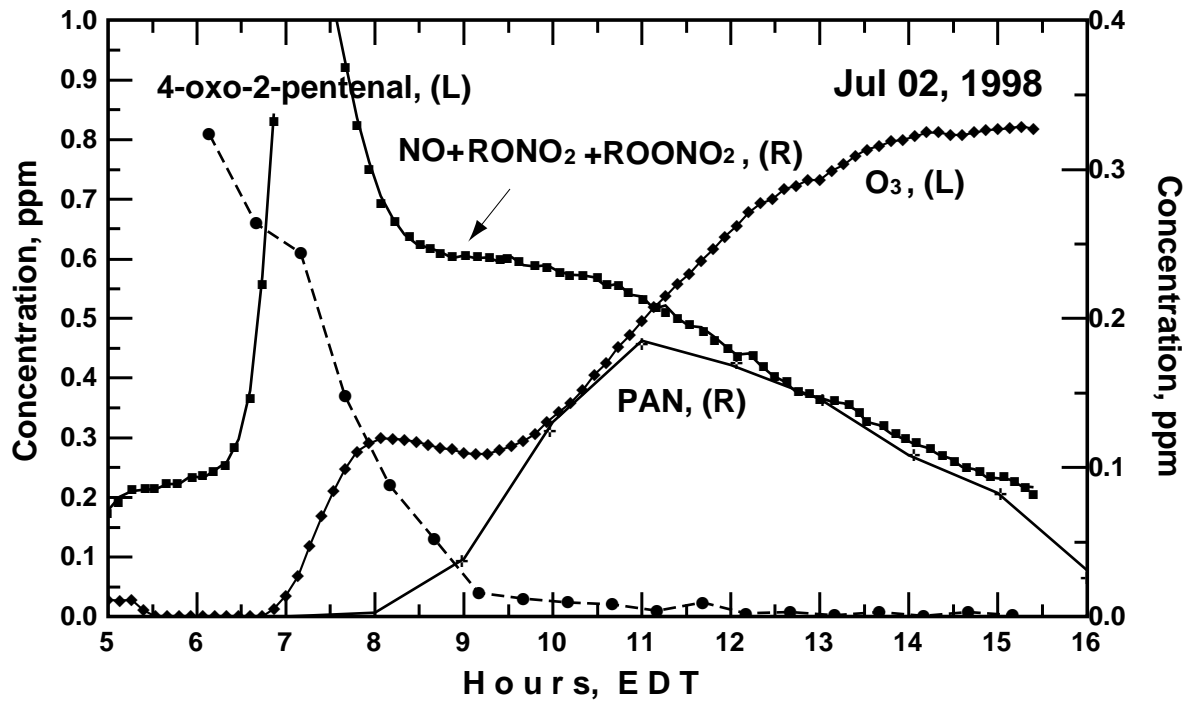


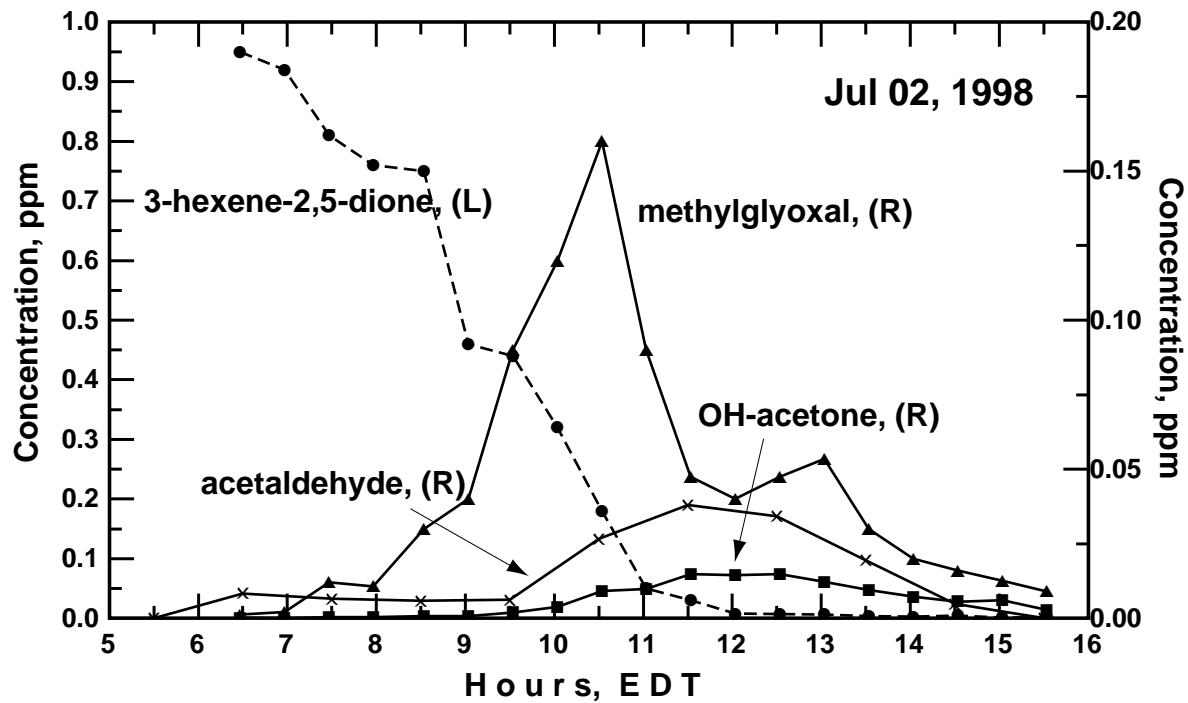


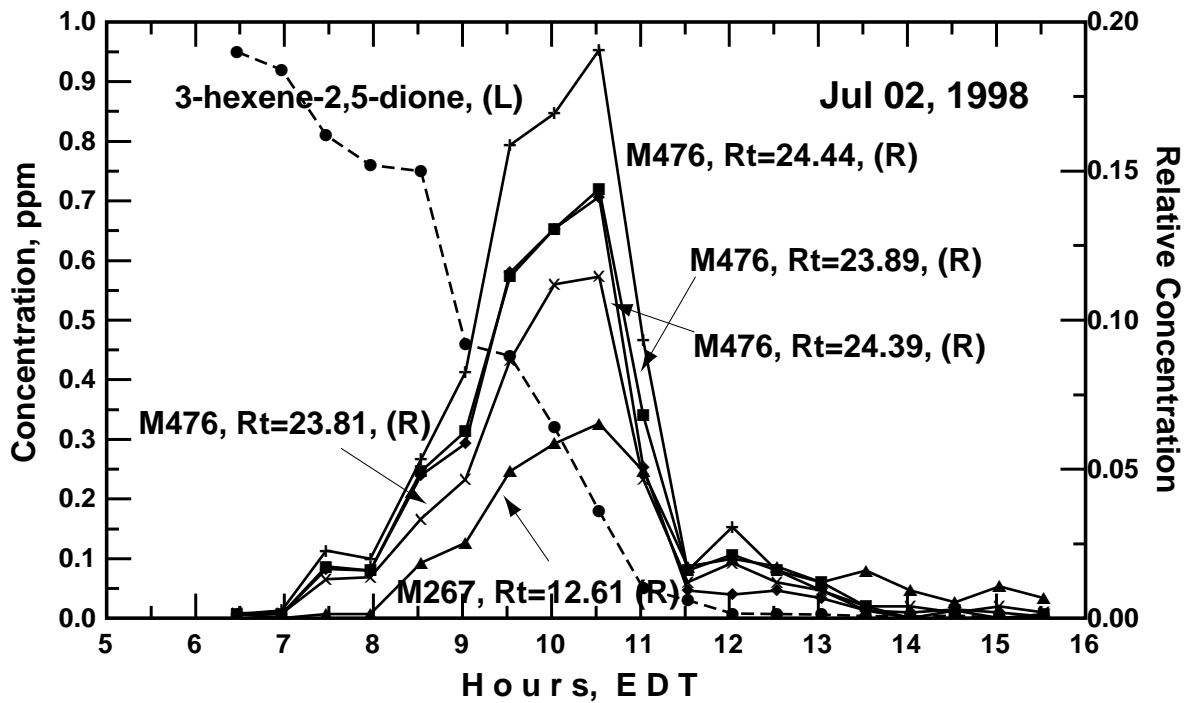


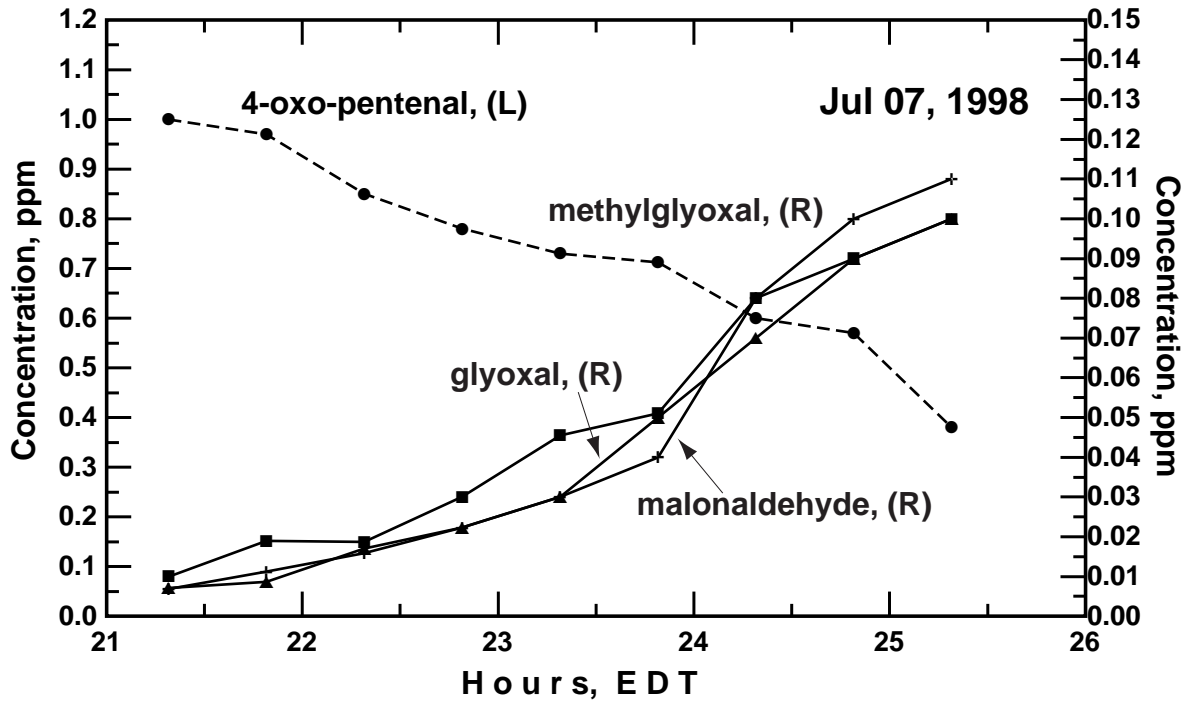


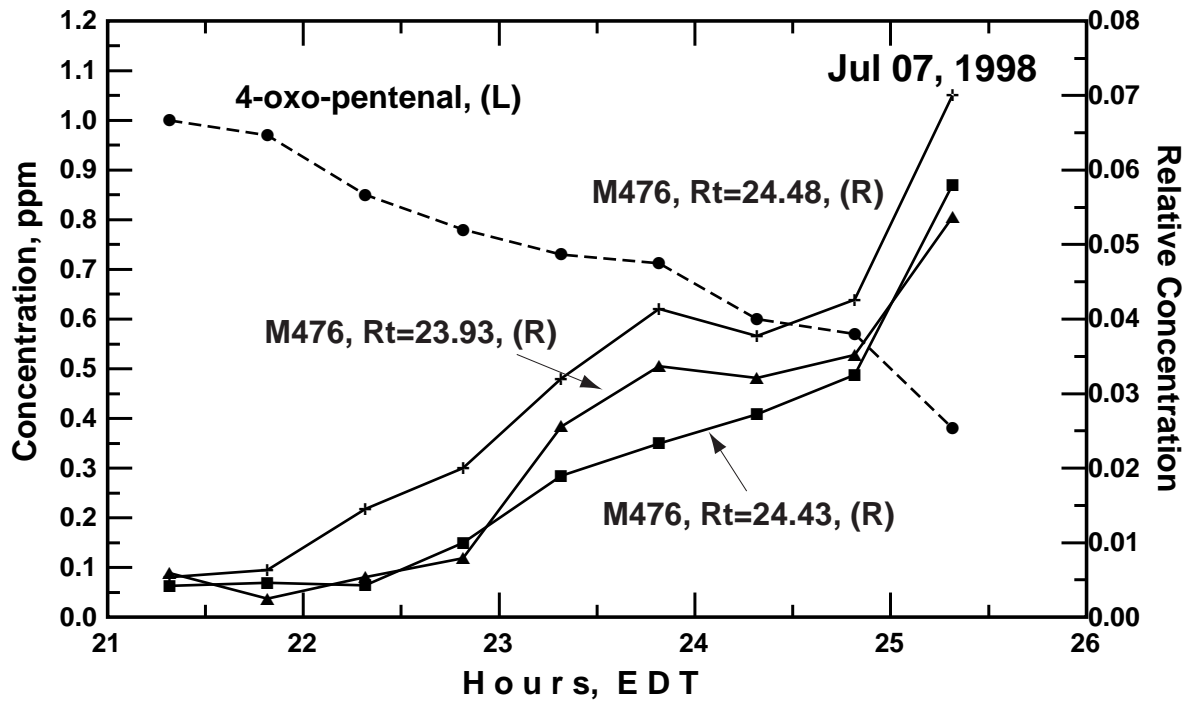


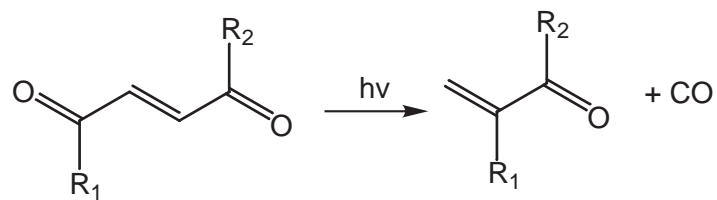




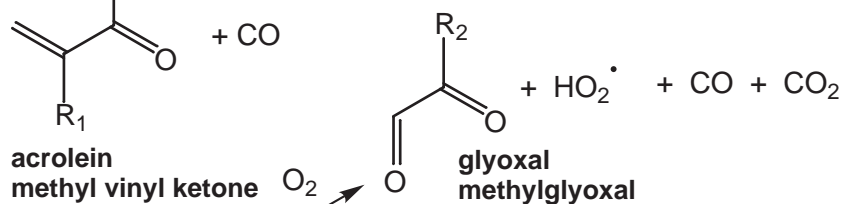




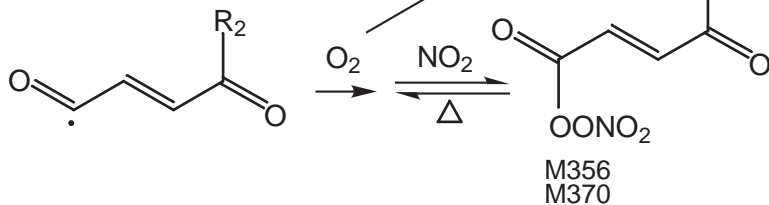




$\text{R}_1=\text{H}, \text{R}_2=\text{H}$, butendial
 $\text{R}_1=\text{H}, \text{R}_2=\text{CH}_3$, 4-oxo-2-pentenal
 $\text{R}_1=\text{CH}_3, \text{R}_2=\text{CH}_3$, 3-hexene-2,5-dione



H abstraction
 (Butendial
 4-Oxo-2-pentenal)



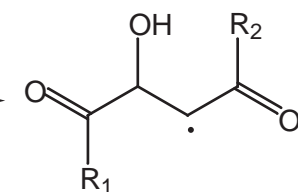
NO

O₂

NO₂

Δ

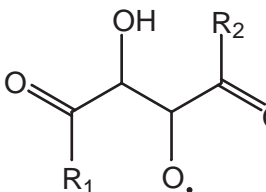
OH, 2,3-addition



O₂

NO

NO₂



O₂

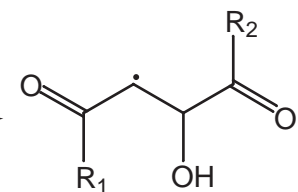
OH

R₂

HO₂[•]

M311, M506
M325, M520
M339, M534

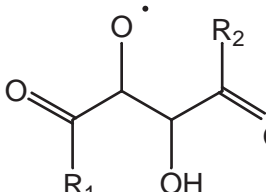
OH, 3,2-addition



O₂

NO

NO₂



O₂

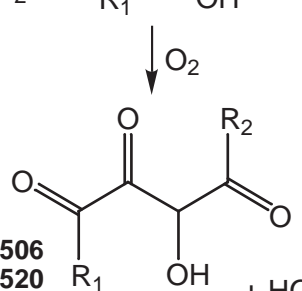
OH

R₂

HO₂[•]

glyoxal
glyoxal, methylglyoxal
methylglyoxal

M311, M506
M325, M520
M339, M534



OH

R₂

HO₂[•]

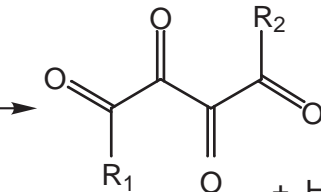
+ H₂O

R₁

O

+ HO₂[•]

M309, M504
M323, M518
M337, M532



O₂

R₂

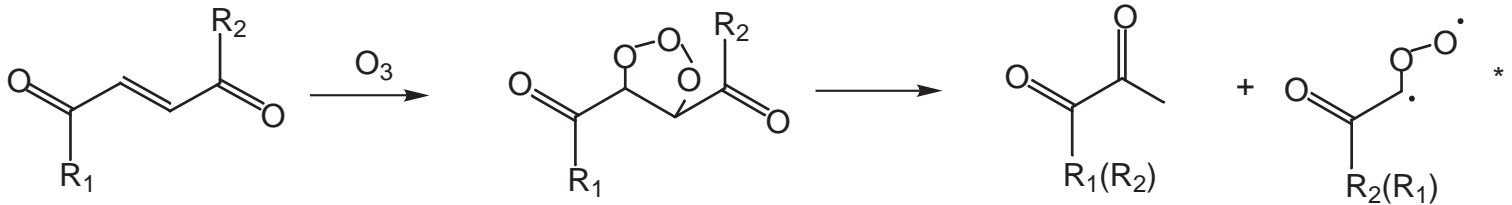
HO₂[•]

+ H₂O

R₁

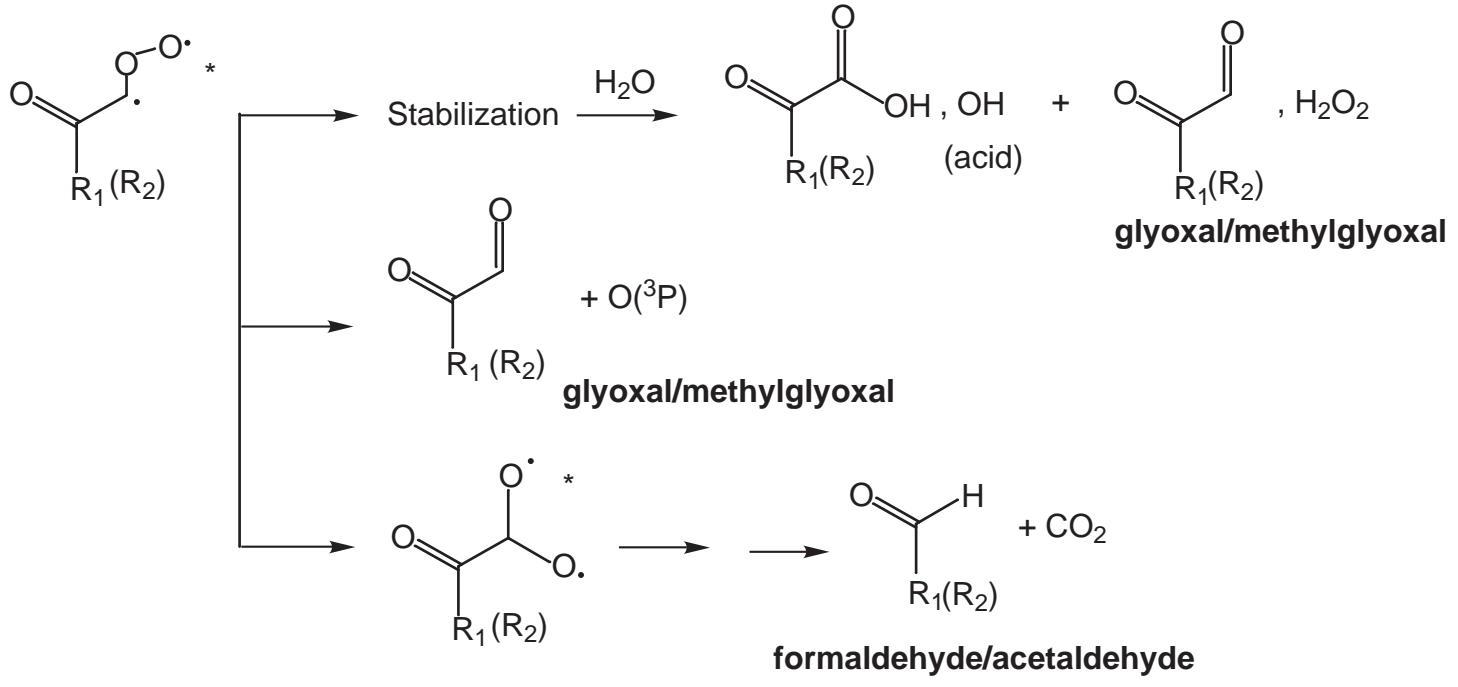
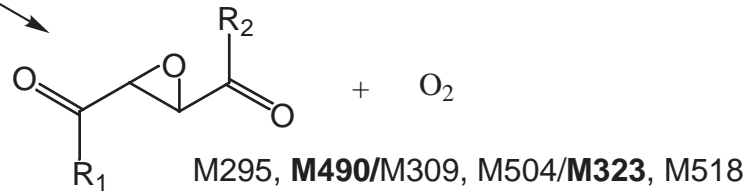
O

+ HO₂[•]



$R_1=H, R_2=H$, butendial
 $R_1=H, R_2=CH_3$, 4-oxo-2-pental
 $R_1=CH_3, R_2=CH_3$, 3-hexene-2,5-dione

glyoxal/methylglyoxal



glyoxal/methylglyoxal

glyoxal/methylglyoxal

formaldehyde/acetaldehyde

TABLE 1. Reaction Conditions for the 1,4-unsaturated Dicarbonyls UNC Outdoor Smog Chamber Experiments

date	hydrocarbon (HC)	side ^a	time(EDT)	concentrations			temperature (K)	
				HC (ppmV)	NO _x (ppm)	O ₃ (ppm hr ⁻¹)	chamber	dewpoint
Oc0697	butenedial	RED	0716-1630	0.7	0.64		283-306	283-286
Oc1397	butenedial	BLUE	0722-1600	1.5	0.6		283-303	277-281
Jn1898	4-oxo-2-pentenal	RED	0600-1500	1.5	0.6		290-311	288-290
Jn1898	butenedial	BLUE	0600-1500	1	0.6		290-311	288-290
JI0298	4-oxo-2-pentenal	RED	0604-1530	0.8	0.6		291-311	288-290
JI0298	3-hexene-2,5-dione	BLUE	0604-1530	0.8	0.6		291-311	288-290
JI0798	4-oxo-2-pentenal / cyclohexane	BLUE	2050-0130	1/150		0.33	297-293	290-290
JI0798	cyclohexane	RED	2050-0130	150		0.33	297-293	290-290
Au1898	butenedial / cyclohexane	BLUE	2052-0200	1/100		0.33	298-294	291-292
Au1898	cyclohexane	RED	2052-0200	100		0.33	298-294	291-292
Au2598	3-hexene-2,5-dione/cyclohexane	BLUE	2014-0140	0.9/100		0.33	297-295	291-292
Au2598	cyclohexane	RED	2014-0140	100		0.33	297-295	291-292
St1598	4-oxo-2-pentenal / cyclohexane	BLUE	2105-0140	0.9/100		0.33	294-291	290-290
St1598	3-hexene-2,5-dione/cyclohexane	RED	2105-0140	0.9/100		0.33	294-291	290-290

^a RED and BLUE are used to distinguish the chamber side

TABLE 2. Possible Structures of Unidentified Carbonyls with Known Molecular Weight

MW^a	FW^b	possible structure	reactants
M267	72	C ₃ unsaturated hydroxy carbonyls, C ₃ dicarbonyls, C ₃ epoxy carbonyls, C ₄ saturated carbonyls (can not be isobutyraldehyde, butyraldehyde, methyl ethyl ketone, glycidaldehyde, methylglyoxal, or malonaldehyde)	4-oxo-2-pentenal
M281	86	C ₄ unsaturated hydroxy carbonyls, C ₄ epoxy carbonyls, C ₄ dicarbonyls, C ₃ triones, C ₅ saturated carbonyl, C ₄ cyclic carbonyl (can not be biacetyl)	4-oxo-2-pentenal
M283	88	C ₄ hydroxy carbonyls, C ₃ hydroxy dicarbonyls	butenedial 4-oxo-2-pentenal
M297/M492 ^c	102	C ₄ hydroxy dicarbonyls (M297 can also be C ₅ hydroxy carbonyls but can not be 3-hydroxy-3-methyl-2-butanone, 4- hydroxy-3-methyl-2-butanone, and 5-hydroxy-2-pentanone)	4-oxo-2-pentenal 3-hexene-2,5-dione
M309/M504 ^c	114	C ₄ quadra-ones, C ₅ triones, C ₅ epoxy dicarbonyls C ₆ dicarbonyl (M309 can also be C ₆ unsaturated hydroxy carbonyl)	3-hexene-2,5-dione 4-oxo-2-pentenal
M311/M506 ^c	116	C ₄ hydroxy triones, C ₅ hydroxy dicarbonyls (M311 can also be C ₆ hydroxy carbonyls, but can not be 4-hydroxy-4-methyl-2-pentanone)	butenedial 4-oxo-2-pentenal
M323	128	C ₅ quadra-ones, C ₆ epoxy dicarbonyls	4-oxo-2-pentenal
M325/M520 ^c	130	C ₅ hydroxy triones	4-oxo-2-pentenal 3-hexene-2,5-dione
M328	133	unknown	4-oxo-2-pentenal

TABLE 2. Possible Structures of Unidentified Carbonyls with Known Molecular Weight (continued)

MW^a	FW^b	possible structure	reactants
M476	86	C ₃ triones, C ₄ dicarbonyls (can not be biacetyl)	butenedial 4-oxo-2-pentenal 3-hexene-2,5-dione
M490	100	C ₄ triones, C ₄ epoxy dicarbonyls, C ₅ dicarbonyl and C ₄ unsaturated hydroxy dicarbonyl (can not be 2,4-pentadione)	4-oxo-2-pentenal 3-hexene-2,5-dione
M502	112	C ₆ unsaturated dicarbonyl (can not be 3-hexene-2,5-dione)	butenedial

^a molecular weight of the PFBHA derivative; ^b molecular weight of carbonyl

^c the first number is the molecular weight of the PFBHA mono-derivative, the second number is that of the PFBHA di-derivative

TABLE 3. Carbonyl Products Detected in the Batch Sample Collected from O₃-Initiated 1,4-unsaturated Dicarboxyls Outdoor Smog Chamber Experiments
(M numbers are molecular weight of the PFBHA derivative)

Compound	products
Butenedial	formaldehyde, glyoxal, methylglyoxal M490, M476, M506
4-oxo-2-pentenal ^a	formaldehyde, glyoxal, methylglyoxal, malonaldehyde M267, M309, M325, M476, M502, M520
3-hexene-2,5-dione ^a	formaldehyde, methylglyoxal, M476, M490, M504

^aCyclohexanone also detected (from cyclohexane added as OH radical scavenger)

TABLE 4. Comparison of Rate Constants for 1,4-Unsaturated Dicarbonyls with O₃

compounds	kO₃ (10⁻¹⁸ x cm³ molecule⁻¹s⁻¹)	temperature (K)	references
Butenedial*	1.6±0.1	294-298	this work
cis-butenedial	2	296	(3)
trans-butenedial	2	296	(3)
4-oxo-2-pentenal*	4.8±0.8	293-297	this work
cis-4-oxo-2-pentenal	2	296	(3)
trans-4-oxo-2-pentenal	2	296	(3)
3-hexene-2,5-dione*	3.6±0.3	295-297	this work
cis-3-hexene-2,5-dione	1.8±0.2	298±2	(4)
trans-3-hexene-2,5-dione	8.3±1.2	298±2	(4)

* mixture of cis- and trans-