*Environ. Sci. Technol.* **1994**, *28*, 715–729

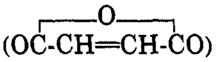
# Atmospheric Chemistry of Unsaturated Carbonyls: Butenedial, 4-Oxo-2-pentenal, 3-Hexene-2,5-dione, Maleic Anhydride, 3*H*-Furan-2-one, and 5-Methyl-3*H*-furan-2-one

**Arwid Bierbach, Ian Barnes,* Karl H. Becker, and Evelyn Wiesen**

Physikalische Chemie/Fachbereich 9, Bergische Universität, GH Wuppertal, D-42097 Wuppertal, FRG

As part of a study on the oxidation mechanisms of aromatics some aspects of the atmospheric chemistry of several possible products, unsaturated 1,4-dicarbonyl compounds and two furanones, have been investigated in a 1080-L reaction chamber by 296 ± 2 K in 1000 mbar of synthetic air. Rate coefficients for the reaction of OH radicals with the following compounds have been obtained using the relative method (in units of $10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$): *cis*-butenedial (maleic dialdehyde), 52.1 ± 1.0; *trans*-butenedial (fumaric dialdehyde), ≥24.1 ± 7.9; *cis*/*trans*-4-oxo-2-pentenal (acetylacrolein), 55.8 ± 2.1; *cis*-3-hexene-2,5-dione, 69.0 ± 21.0; *trans*-3-hexene-2,5-dione, 40.0 ± 4.0; maleic anhydride, 1.45 ± 0.1; 3*H*-furan-2-one, 44.5 ± 2.6; 5-methyl-3*H*-furan-2-one (α-angelica lactone), 69.0 ± 4.6. The first gas-phase FTIR spectra of *cis*-butenedial, *trans*-butenedial, *cis*/*trans*-4-oxo-2-pentenal, and 3*H*-furan-2-one are presented. The photochemistry of the dicarbonyls is discussed, and preliminary results from product studies on the OH-initiated oxidation of the dicarbonyl compounds are reported. The results indicate that reaction with OH radicals will be an important atmospheric sink for all of the unsaturated carbonyls studied here. However, for butenedial, 4-oxo-2-pentenal, and hexene-2,5-dione the results suggest that photolysis will probably be an even stronger sink.

## Introduction

In product studies of the OH-initiated oxidation of aromatic hydrocarbons in this and other laboratories (*1–5*, and references cited therein) evidence has been found for the formation of unsaturated 1,4-dicarbonyls with the general structure $R_1$-CO-CH=CH-CO-$R_2$ where $R_1$ and $R_2$ can either be H atoms or alkyl groups. Bandow et al. (*6, 7*) were the first to identify maleic anhydride  $(\overset{\ulcorner\text{—O—}\urcorner}{\text{OC-CH=CH-CO}})$ in FTIR product studies of the OH-initiated oxidation of benzene, toluene, and the xylene isomers. They postulated the unsaturated 1,4-dicarbonyl butenedial (OHC-CH=CH-CHO) to be the anhydride's precursor but could not prove this experimentally. With the exception of 4-oxo-2-pentenal ($CH_3$-CO-CH=CH-CHO) (*1, 2*) and 3-hexene-2,5-dione ($CH_3$-CO-CH=CH-CO-$CH_3$) (*1, 2, 6–10*), which have been identified directly in aromatic oxidation systems using FTIR, the formation of other aliphatic unsaturated dicarbonyls has only been implied from mass spectroscopic analyses of aromatic oxidation systems.

The mechanism of the formation of ring-opening products in the OH-initiated degradation of aromatic hydrocarbons is still very speculative. Kinetic studies (*11*) indicate that under atmospheric conditions the primary step involves addition of the OH radical to the aromatic ring with subsequent reaction of the adduct with $O_2$ to form hydroxycyclohexadienylperoxy radicals. The fate of these peroxy radicals is still a matter of intensive research, suggested possibilities include (i) ring opening with the formation of hexadienedials; (ii) cyclization of the hydroxycyclohexadienylperoxy radical, forming a bicyclic radical with subsequent addition of a second $O_2$, and then further reaction to products; and (iii) rearomatization with formation of phenolic compounds and $HO_2$. Secondary reactions can be formulated for both processes i and ii that can account for the formation of unsaturated dicarbonyls with the structure $R_1$-OC-CH=CH-CO-$R_2$. FTIR product studies currently in progress in this laboratory on the OH-initiated oxidation of the cresols and mono- and dialkylated phenols show that unsaturated 1,4-dicarbonyls are also important products of these systems. Therefore, the further oxidation of any phenols formed in the oxidation of benzene, toluene, and the xylenes also represents a source of unsaturated 1,4-dicarbonyls. The relative importance of the possible pathways leading to unsaturated 1,4-dicarbonyl formation is presently highly uncertain.

Of the unsaturated 1,4-dicarbonyls which can be formed in the oxidation of aromatics, only the atmospheric chemistry of 3-hexene-2,5-dione appears to have been studied to date (*8–10*). Since such compounds appear to be important products of both alkylated benzenes and alkylated phenols, the unsaturated 1,4-dicarbonyls *cis*-butenedial (maleic dialdehyde), *trans*-butenedial (fumaric dialdehyde), *cis*/*trans*-4-oxo-2-pentenal (acetylacrolein), *cis*-3-hexene-2,5-dione, and *trans*-3-hexene-2,5-dione have been synthesized, and some aspects of their atmospheric chemistry have been investigated: photolysis and reaction with OH radicals. During the course of the studies, it became evident that maleic anhydride, 3*H*-furan-2-one, and 5-methyl-3*H*-furan-2-one (α-angelica lactone) are important products of the oxidation processes of the unsaturated 1,4-dicarbonyls under atmospheric conditions, and consequently the kinetics and products of the OH-initiated oxidation of these compounds were also investigated.

## Experimental Section

**Kinetic and Product Studies.** The experiments concerning the kinetic and product studies of the various unsaturated carbonyl compounds were carried out in an 1080-L quartz-glass chamber, which is surrounded by 32 low-pressure mercury lamps (UV lamps, $\lambda_{max}$ = 254 nm) and 32 super actinic fluorescent lamps (VIS lamps, 320 ≤ λ ≤ 480 nm, $\lambda_{max}$ = 360 nm). Details of the experimental setup can be found elsewhere (*12*). The concentration–time profiles of reactants and products were monitored in situ by long-path FTIR using an optical path length of 492 m and a spectral resolution of 1 cm$^{-1}$. The reactants were monitored at the following absorption frequencies (in cm$^{-1}$): *cis*-butenedial, 1702; *trans*-butenedial, 1724; *cis*/*trans*-4-oxo-2-pentenal, 1700–1720; *cis*-3-hexene-2,5-

0013-936X/94/0928-0715$04.50/0

dione, 1170 and 1720; *trans*-3-hexene-2,5-dione, 1250 and 1705; maleic anhydride, 1805; 3*H*-furan-2-one, 1834; propene, 2954 and 912; *n*-butane, 2966.

The experiments were performed at a total pressure of 1000 mbar synthetic air and a temperature of 296 ± 2 K using irradiation times between 10 and 300 min. The 254-nm photolysis of $H_2O_2$ was used as the OH source:

$$H_2O_2 + h\nu\ (\lambda = 254\ \text{nm}) \rightarrow 2\text{OH}$$

The concentration of $H_2O_2$ was typically $\approx 10^{15}$ molecules $\text{cm}^{-3}$. The concentrations of the carbonyls and the reference hydrocarbons *n*-butane and propene were in the range $0.5\text{–}1 \times 10^{14}$ molecules $\text{cm}^{-3}$. The kinetic data for the reaction of OH with 5-methyl-3*H*-furan-2-one were obtained in a 20-L glass reactor (Duran borosilicate glass 3.3 supplied by Schott, FRG) relative to *trans*-2-butene under similar conditions to those in the 1080-L reactor using the photolysis of $CH_3ONO$ with four super actinic fluorescent lamps as the OH radical source (*13*). This reaction was carried out in the 20-L reactor due to the unavailability of the 1080-L reactor at the time of the experiment. The concentration–time behavior of both substances were followed over a 15–30-min time period by gas chromatography with FID detection after separation on a 2-m 1/4-in. stainless steel column filled with Carbowax 600 on Chromosorb PAW (100/120) at a temperature of 323 K. In experiments using $CH_3ONO/NO_x$ systems as the OH radical source, interference due to reactions with $O(^3P)$ atoms formed in the photolysis of $NO_2$ can occur (*14*). However, there are several factors which suggest that interference due to $O(^3P)$ reactions is minimal. First, the $NO_2$ photolysis rate is relatively low, and second, O atom reactions with alkenes result in relatively high yields of epoxide-type compounds, which were not detected in the product analyses. Finally, in the reaction system, the concentration of $NO_2$ increases with time, this would be expected to result in increasing concentrations of $O(^3P)$ atoms with time. Such an O atom increase, if significant, would be expected to lead to curvature in plots of the kinetic data. As discussed below, no such curvature was observed in plots of the kinetic data.

The OH radicals generated in the photolysis systems will react with the carbonyls and also the reference hydrocarbon:

$$\text{OH} + \text{carbonyl} \rightarrow \text{products},\ k_1$$

$$\text{OH} + \text{reference} \rightarrow \text{products},\ k_2$$

Under the experimental conditions, the carbonyls can additionally undergo photodissociation and may also be lost to the chamber walls. These first-order loss processes can be represented by:

$$\text{carbonyl} + h\nu \rightarrow \text{products},\ k_3$$

$$\text{carbonyl} + \text{wall} \rightarrow \text{products},\ k_4$$

The reference hydrocarbons do not photolyze at 254 nm, and wall losses for these compounds were found to be negligible. Provided that the compounds are not re-formed in the reaction system, the decay of the carbonyls and the reference hydrocarbons will be governed by the rate laws I and II, respectively, which can be rearranged to give eq III:

$$-\frac{d[\text{carbonyl}]}{dt} = k_1[\text{OH}][\text{carbonyl}] + (k_3 + k_4)[\text{carbonyl}] \qquad \text{(I)}$$

$$-\frac{d[\text{reference}]}{dt} = k_2[\text{OH}][\text{reference}] \qquad \text{(II)}$$

$$\ln\left\{\frac{[\text{carbonyl}]_{t_0}}{[\text{carbonyl}]_t}\right\} - (k_3 + k_4)(t - t_0) = \frac{k_1}{k_2}\ln\left\{\frac{[\text{reference}]_{t_0}}{[\text{reference}]_t}\right\} \qquad \text{(III)}$$

If the term $k_3 + k_4$ is zero or negligibly small, then plots of $\ln\{[\text{carbonyl}]_{t_0}/[\text{carbonyl}]_t\}$ versus $\ln\{[\text{reference}]_{t_0}/[\text{reference}]_t\}$ should give straight lines with slopes of $k_1/k_2$ and zero intercept. If, however, the term $k_3 + k_4$ is nonnegligible, then eq III can be rearranged to give eq IV:

$$\frac{1}{(t - t_0)}\ln\left\{\frac{[\text{carbonyl}]_{t_0}}{[\text{carbonyl}]_t}\right\} = \frac{1}{(t - t_0)}\frac{k_1}{k_2}\ln\left\{\frac{[\text{reference}]_{t_0}}{[\text{reference}]_t}\right\} + (k_3 + k_4) \qquad \text{(IV)}$$

Plots of $1/(t - t_0)\ \ln\{[\text{carbonyl}]_{t_0}/[\text{carbonyl}]_t\}$ versus $1/(t - t_0)\ \ln\{[\text{reference}]_{t_0}/[\text{reference}]_t\}$ should give a straight line with a slope of $k_1/k_2$ and an intercept of $k_3 + k_4$. With the exception of the kinetic measurements on 5-methyl-3*H*-furan-2-one, which was performed in the small 20-L glass vessel, all of the other compounds were investigated in the large reactor. Although wall losses were observed on injecting the compounds into the large reactor, after stabilization with buffer gas, wall losses were generally very low and often below the detection limit on the time scale of the experiments. In comparison, the wall loss of 5-methyl-3*H*-furan-2-one in the small 20-L reactor was relatively high. The measured wall losses for all the compounds are listed in Table 1. Due to the low wall loss rates of the compounds, the intercepts of plots according to eq IV will, in most cases, reflect the photolysis frequency $k_3$.

**Methods of Preparation of Unsaturated Dicarbonyls and Their Gas-Phase FTIR Spectra.** The various carbonyl compounds investigated were either synthesized directly or produced in situ in the reactor by photolysis or reaction of a suitable precursor. Due to the complicated nature of the method of preparation, it has not been possible to obtain reliable IR absorption coefficients for the majority of the carbonyl compounds, and as a consequence, calculation of the absolute yields of photolysis and OH reaction products has also not been possible; in some instances, however, as outlined in the Results and Discussion section, estimations have been possible.

(*A*) *Butenedial Isomers and 3H-Furan-2-one.* A mixture of butenedial isomers was prepared by the oxidative ring-opening of 2,5-dimethyl-2,5-dihydrofuran with $H_2SO_4$ as described by Hufford et al. (*15*). This procedure results in a 2,5-dimethyl-2,5-dihydrofuran solution containing *cis*-butenedial (maleic dialdehyde) and *trans*-butenedial (fumaric dialdehyde). Approximately 70% of the butenedial is initially in the cis form; absolute yields cannot be obtained since the solution slowly decomposes. The solution also contains traces of methanol and 3*H*-

**Table 1. Rate Coefficient Ratios $k_1/k_2$, First-Order Photolysis Loss Rates $k_3$, Wall Loss Rates $k_4$, and Rate Coefficients $k_1$ for Reaction of OH Radicals with Furanones and Unsaturated Dicarbonyls at 296 ± 2 K in 1000 mbar of Synthetic Air**

| compound | $k_1/k_2$ | $k_3$ ($10^{-4}$ s$^{-1}$) | $k_4$ ($10^{-4}$ s$^{-1}$) | $k_1 \times 10^{12}$ (cm$^3$ molecule$^{-1}$ s$^{-1}$) | technique[a] | reference | literature |
|---|---|---|---|---|---|---|---|
| *cis*-butenedial | 1.99 ± 0.04[b] | 5.8 ± 0.2 | <0.05 | 52.1 ± 1.0 | CP-FTIR | propene | this work |
| *trans*-butenedial | ≥0.92[b] | 3.9 ± 0.3 | <0.05 | ≥24.1 | CP-FTIR | propene | this work |
| *cis*/*trans*-4-oxo-2-pentenal | 2.13 ± 0.08[b] | 3.7 ± 0.2 | <0.05 | 55.8 ± 2.1 | CP-FTIR | propene | this work |
| *cis*-3-hexene-2,5-dione | 2.56 ± 0.78[b] | ~8.3 | 0.17 ± 0.03 | 69.0 ± 21 | CP-FTIR | propene | this work |
|  | 2.40 ± 0.23[c] |  |  | 63.0 ± 6.0 | CP-FTIR | propene | Tuazon et al. (*8*) |
| *trans*-3-hexene-2,5-dione | 1.48 ± 0.15[b] | 8.1 ± 0.9 | 0.17 ± 0.03 | 40.0 ± 4.0 | CP-FTIR | propene | this work |
|  | 2.02 ± 0.09[c] |  |  | 53.0 ± 3.0 | CP-FTIR | propene | Tuazon et al. (*8*) |
| maleic anhydride | 0.58 ± 0.03[b] | 1.0 ± 0.2 | <0.05 | 1.45 ± 0.1 | CP-FTIR | *n*-butane | this work |
| 3*H*-furan-2-one | 1.68 ± 0.10[b] | negligible | <0.05 | 44.5 ± 2.6 | CP-FTIR | propene | this work |
| 5-methyl-3*H*-furan-2-one | 1.06 ± 0.07[c] | negligible | 2.0 ± 0.3 | 69.0 ± 4.6 | CP-GC | *trans*-2-butene | this work |

[a] Technique: CP-FTIR, continuous photolysis-Fourier transform infrared spectroscopy; CP-GC, continuous photolysis-gas chromatography. [b] The 254-nm photolysis of $H_2O_2$ was used as the OH radical source. [c] The photolysis of $CH_3ONO$/NO/air (320 ≤ λ ≤ 480 nm, $\lambda_{max}$ = 360 nm) was used as the OH radical source.

furan-2-one. An IR spectrum consisting of approximately 70% *cis*-butenedial and 30% *trans*-butenedial was obtained by injection of the synthesis solution into the reactor and by subtraction of absorptions due to the solvent, methanol, and 3*H*-furan-2-one (Figure 1; spectrum 1a). Other work in this laboratory (*16*) on the OH-initiated oxidation in furan in 1000 mbar of synthetic air at 296 K using the 254-nm photolysis of $H_2O_2$ as the OH radical source has shown that *trans*-butenedial is a major product. Figure 1 (spectrum 1b) shows an IR spectrum that was obtained after 10-min irradiation of a furan/$H_2O_2$/air reaction system and subtraction of the absorptions from the reactants furan and $H_2O_2$ and the products CO, $CO_2$, HCHO, HCOOH, ketene, glyoxal, and maleic anhydride. This spectrum is essentially due to *trans*-butenedial with traces of the cis isomer and 3*H*-furan-2-one. Irradiation of a gas-phase sample of a butenedial synthesis solution for 90 min in 1000 mbar of $N_2$ with the VIS lamps results predominantly in the formation of 3*H*-furan-2-one. Figure 1 (spectrum 1c) shows a product spectrum from such an experiment after subtraction of contributions from the solvent 2,5-dimethyl-2,5-dihydrofuran and the products CO, $CO_2$, HCHO, and HCOOH. Apart from 3*H*-furan-2-one, traces of *cis*/*trans*-butenedial are also detectable in the spectrum.

To obtain "clean" gas-phase FTIR spectra of *cis*-butenedial, *trans*-butenedial, and 3*H*-furan-2-one compounds, i.e., spectra free from contributions of the other two compounds, the following iterative procedure of spectral subtraction was used:

*cis*-butenedial (maleic dialdehyde) =
(spectrum 1a) − (spectrum 1b) − (spectrum 1c)

*trans*-butenedial (fumaric dialdehyde) =
(spectrum 1b) − (*cis*-butenedial) − (spectrum 1c)

3*H*-furan-2-one =
(spectrum 1c) − (*cis*-butenedial) − (*trans*-butenedial)

The clean spectra thus obtained for *cis*-butenedial, *trans*-butenedial, and 3*H*-furan-2-one are shown in Figure 2, panels a–c, respectively.

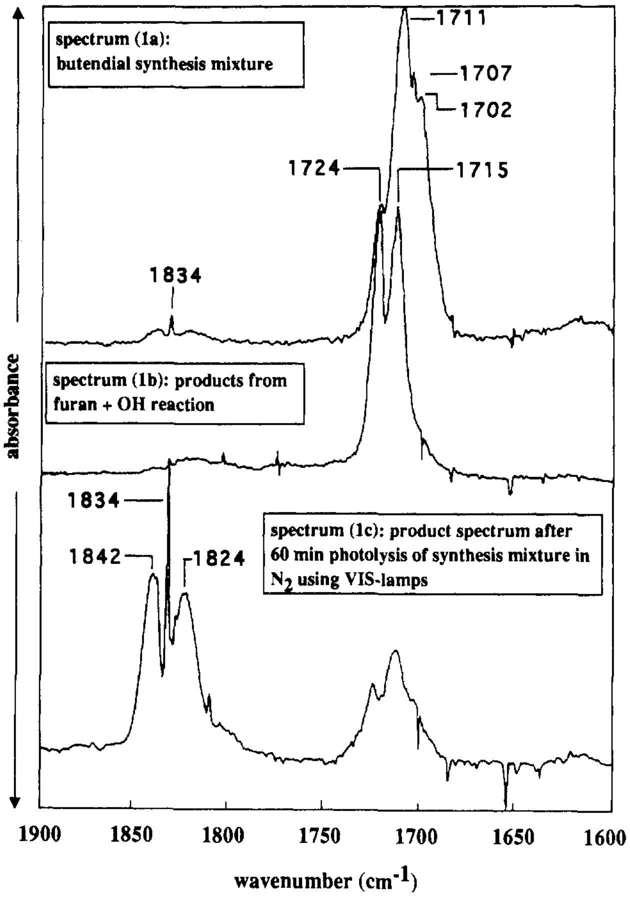


**Figure 1.** (a) Infrared spectrum of the synthesis mixture of butenedial after subtraction of the absorptions due to the solvent 2,5-dimethoxy-2,5-dihydrofuran and traces of $CH_3OH$. The spectrum is comprised of approximately 70% *cis*-butenedial, the trans isomer, and also low concentrations of 3*H*-furan-2-one. (b) Product spectrum obtained after 254-nm irradiation of a furan/$H_2O_2$ mixture in 1000 mbar of air and subtraction of absorptions from furan and the products CO, $CO_2$, HCHO, HCOOH, ketene, glyoxal, and maleic anhydride. The spectrum is predominantly due to *trans*-butenedial with traces of the *cis* isomer and 3*H*-furan-one. (c) Spectrum obtained after 90-min irradiation of the butenedial synthesis mixture with the VIS lamps and subtraction of absorptions from the solvent 2,5-dimethoxy-2,5-dihydrofuran and the products CO, $CO_2$, HCHO, and HCOOH. The spectrum is mainly due to 3*H*-furan-2-one with traces of *cis*/*trans*-butenedial.

(*B*) *4-Oxo-2-pentenal Isomers and 5-Methyl-3H-furan-2-one.* The oxidative ring-opening of 2,5-dimethoxy-2-methyl-5-dihydrofuran with $H_2SO_4$ (*15*) results in a solution containing mainly *cis*-4-oxo-2-pentenal and minor amounts of 5-methyl-3*H*-furan-2-one (α-angelica lactone). Figure 3a shows the residual IR spectrum obtained after subtraction of absorptions due to the solvent 2,5-dimethoxy-2-methyl-5-dihydrofuran and 5-methyl-3*H*-furan-2-one from an IR spectrum of the synthesis solution. This spectrum is primarily due to *cis*-4-oxo-2-pentenal.

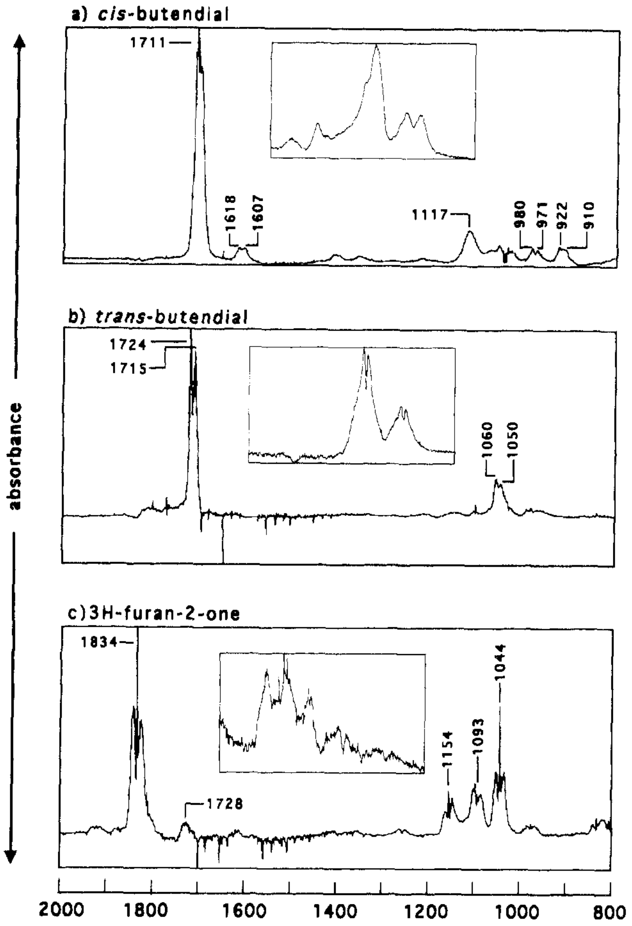


**Figure 2.** Infrared spectra in the range 2000–800 cm$^{-1}$ of (a) *cis*-butenedial, (b) *trans*-butenedial, and (c) 3*H*-furan-2-one; see text for details of the procedure used to obtain the clean spectra. The insets show the spectral range 3100–2600 cm$^{-1}$.

The trans isomer can be prepared in situ by photolysis of the cis isomer with the fluorescent lamps. However, investigations in this laboratory have shown that the ozonolysis of *trans,trans*-3,5-heptadien-2-one gives *trans*-4-oxo-2-pentenal as a major product (*17*). Figure 3b shows the residual spectrum, which is obtained after 15-min reaction of $O_3$ with *trans,trans*-3,5-heptadien-2-one in 1000 mbar of synthetic air and subtraction of the other products acetaldehyde, methylglyoxal, and crotonaldehyde. The residual spectrum is due mainly to *trans*-4-oxo-2-pentenal. 5-Methyl-3*H*-furan-2-one is commercially available and was purchased from Aldrich with a stated purity of 98%; its IR spectrum is shown in Figure 3c.

(*C*) *3-Hexene-2,5-dione Isomers.* Ring cleavage of 2,5-dimethylfuran with cerium(IV) ammonium nitrate was used to synthesize *trans*-3-hexene-2,5-dione directly (*17–19*). Irradiation of the trans isomer with the fluorescent lamps results in an equilibrium mixture of cis/trans isomers (*8–10*). An IR spectrum of the cis isomer was obtained by subtraction of the IR spectrum of the pure trans isomer. The IR spectra of both isomers were in good agreement with those already available in the literature (*8–10*).

## *Results and Discussion*

**OH Kinetics of Unsaturated 1,4-Dicarbonyls, Furanones, and Maleic Anhydride.** Figure 4, panels a–h shows the kinetic data for the unsaturated 1,4-dicarbonyls, furanones, and maleic anhydride investigated plotted according to either eq III or eq IV. Each plot represents a minimum of three experiments. Since the cis/trans isomers of butenedial, 4-oxo-2-pentenal, and hexenedione are photolyzed by the mercury lamps used to generate the OH radicals, the data for these compounds were initially plotted according to eq IV, which also takes into account first-order loss processes such as photolysis and/or wall losses. However, the use of this analysis method resulted in clusters of the experimental points rather than good linear relationships. Such difficulties are often experienced with this method of analysis when the concentration of the OH radical shows very little change with reaction time. Because of the nonlinearity obtained using eq IV, the data for *cis*/*trans*-butenedial, *cis*/*trans*-4-oxo-2-pentenal, and *cis*/*trans*-3-hexene-2,5-dione were plotted using eq III, after determination of the first-order loss processes $k_3$ of the relevant compounds in separate experiments in the absence of OH radicals. The determination of $k_3$ was made in experiments immediately preceding the determination of $k_1$ in order to avoid possible fluctuations in $k_3$ due to changes in reactor conditions. The measured first-order loss rates for *cis*/*trans*-butenedial, *cis*/*trans*-

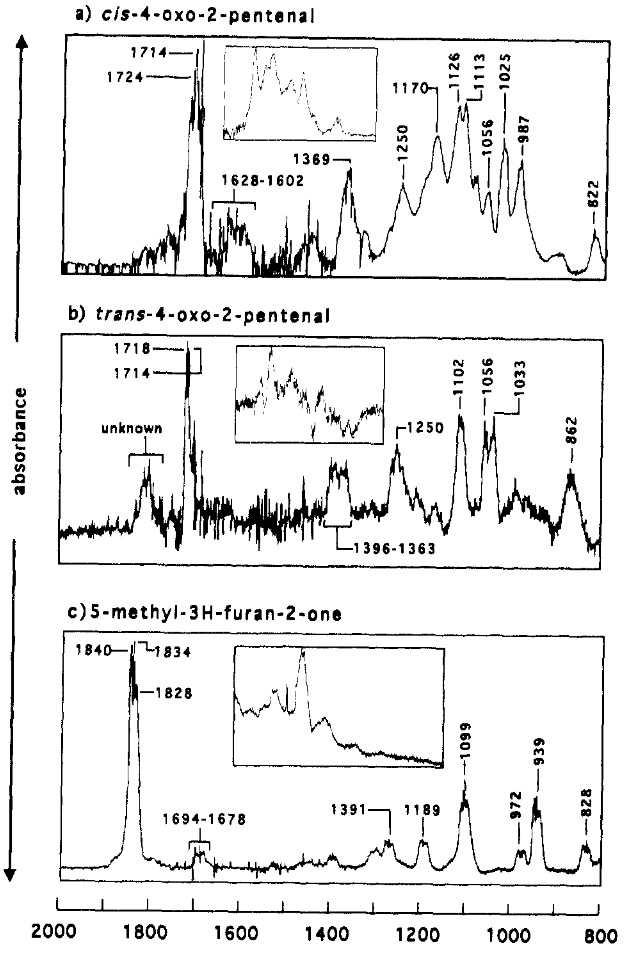


**Figure 3.** Infrared spectra in the range 2000–800 cm$^{-1}$ of the following: (a) the synthesis solution of 4-oxo-2-pentenal in synthetic air after subtraction of absorptions from the solvent 2,5-dimethoxy-2-methyl-5-dihydrofuran and 5-methyl-3*H*-furan-2-one; (b) residual product spectrum obtained after ozonolysis of *trans*/*trans*-3,5-heptadienal-2-one and subtraction of absorptions from identified products; (c) spectrum of pure 5-methyl-3*H*-furan-2-one. The insets in panels a–c show the spectral range 3100–2600 cm$^{-1}$.

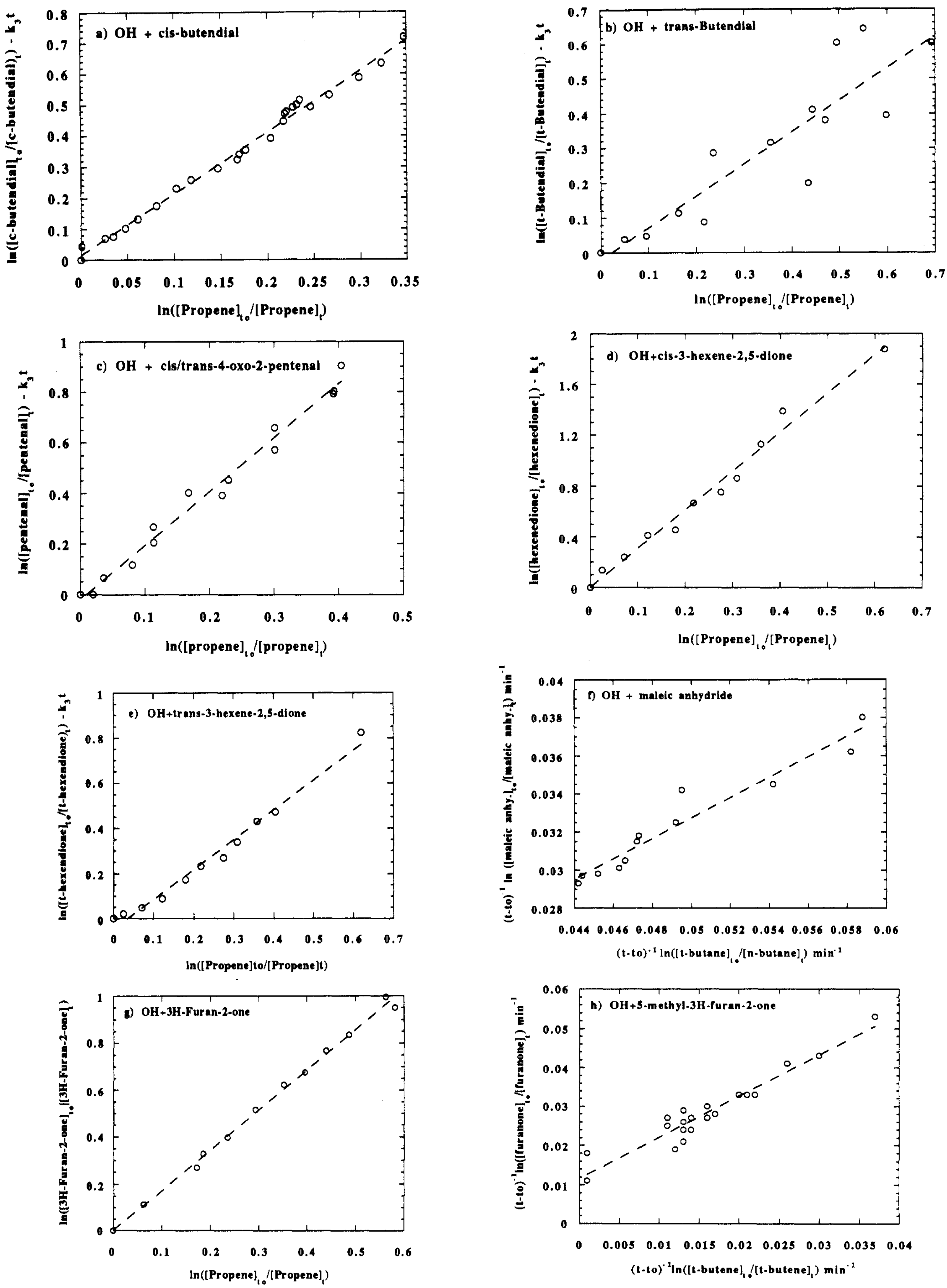


**Figure 4.** Plots of the experimental data for (a) *cis*-butenedial, (b) *trans*-butenedial, (c) *cis/trans*-4-oxo-2-pentenal, (d) *cis*-3-hexene-2,5-dione, (e) *trans*-3-hexene-2,5-dione, (f) maleic anhydride, (g) 3*H*-furan-2-one, and (h) 5-methyl-3*H*-furan-2-one according to either eq III or eq IV as indicated in the text.

4-oxo-2-pentenal, and *cis/trans*-3-hexene-2,5-dione using the UV lamps are listed in Table 1. Since the pure *cis*-3-hexene-2,5-dione isomer was prepared by the photolysis of the pure trans isomer and not synthesized directly, the value for $k_3$ is only an estimate from a study of the cis/trans equilibrium and is therefore subject to a fairly large error. The measured first-order losses were typically $\sim 10^{-4}$ $s^{-1}$ and are attributed mainly to photolysis since wall losses measured in separate experiments were 1 order of magnitude lower. As can be seen from Figure 4, panels a–f, with the exception of *trans*-butenedial, reasonable linearity is obtained when the data for these compounds are plotted according to eq III. The reason for the considerable scatter in the *trans*-2-butenedial data is trans/cis photoisomerization which results in reformation of the trans isomer and makes analysis of the data difficult. Figure 4c represents a common result for both the cis and trans isomers of 4-oxo-2-pentenal since spectral separation between the isomeric forms during the kinetic experiments was not possible. For 3*H*-furan-2-one (Figure 4g), photolysis and wall loss were negligible (i.e., $k_3 \sim 0$), and the data plotted according to eq III show good linearity. The data for maleic anhydride (Figure 4f) and 5-methyl-3*H*-furan-2-one (Figure 4h) were plotted according to eq IV and show reasonable linearity, the axis intercepts are due primarily to photolysis and wall loss, respectively.

The rate cofficients $k_1$ obtained for the various compounds are listed in Table 1, the quoted errors are $\pm 1\sigma$ and represent experimental precision only; uncertainties in the values of the rate coefficients for the reference hydrocarbons have not been taken into consideration. They were calculated from the measured $k_1/k_2$ ratios from the slopes of Figure 4, panels a–h using values of $k_2$ = 2.5, 26.2, and 65.1 × $10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ for the reference hydrocarbons *n*-butane, propene, and *trans*-2-butene, respectively (*20*). In the case of *trans*-butenedial, the determined rate coefficient represents a lower limit because of difficulties in the analysis of the data caused by trans/cis photoisomerization as mentioned above. The rate coefficient for the reaction of OH with *cis*-3-hexene-2,5-dione is subject to a large error due to the uncertainty in the correction for photolysis. Apart from rate coefficient for the reaction of *cis*- and *trans*-3-hexene-2,5-dione with OH (*8*), no other data have been found in the literature for the compounds.

As can be seen from Table 1, the rate coefficients measured for the reactions of OH with *cis*- and *trans*-3-hexene-2,5-dione measured in this study are, despite the difficulties experienced for the cis isomer, in reasonable agreement with the values reported by Tuazon et al. (*8*). The rate coefficients for the reaction of OH with the isomers of butenedial and 4-oxo-2-pentenal are of a similar magnitude to those of 3-hexene-2,5-dione. The values are of the magnitude one would expect for such substances based on a comparison with similar compounds, e.g., the values are slightly more than a factor of 2 higher than the rate coefficients for acrolein and methyl vinyl ketone, which contain similar structural elements to butenedial and 4-oxo-2-pentenal, respectively. The higher rate coefficients measured for butenedial and 4-oxo-2-pentenal compared to either acrolein or methyl vinyl ketone can be attributed to the positive contribution due to H-atom abstraction from the additional terminal CHO group on both compounds. The observed increase is generally between a factor of 1.5–2 higher than would be predicted from structure–reactivity relationships and linear free-energy relationships (*21–25*, and references cited therein). It would appear that the available estimation methods underpredict the effect of two carbonyl functional groups on adjacent ends of the double bond.

The rate coefficient for the reaction of OH with maleic anhydride is 30–40 times lower than the values for the other unsaturated 1,4-dicarbonyls. The rate coefficient is of similar magnitude to those measured for di- and trichloroethenes (*26*, *27*) where the strong negative inductive effect of the Cl atoms reduces the reactivity of the double bond toward electrophilic OH attack. The deactivating effect of the anhydride functional group on the double bond appears to be of similar magnitude to that caused by two or more Cl atoms attached to the double bond. Although this represents the first experimental determination of $k_{OH}$ for maleic anhydride, an estimation of the rate coefficient for this reaction exists in the literature (*21*, *28*, *29*). This estimate is based on structure–reactivity relationships between reaction rate coefficients and ionization potentials (IP) for structural homologues. Using an IP of 9.26 eV, a value of $k$ = 4.3 × $10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ has been estimated for the reaction of OH with maleic anhydride. This value is a factor 30 times higher than the value determined in this study and is more in line with the values measured for the straight-chain unsaturated dicarbonyls. An estimation performed in this laboratory using functional group increments (*22*, *23*) also greatly overpredicts the value of the rate coefficient for the reaction of OH with maleic anhydride. Other techniques of estimation are difficult to apply to this molecule because of the lack of the necessary information. It would appear that the structure–reactivity relying on IP or functional group increments do not satisfactorily take into account the very high deactivating nature of the anhydride functional group.

The rate coefficients for the reaction of OH with the two furanones are of the order of magnitude expected for the ring configuration and show the same reactivity toward OH as the unsaturated dicarbonyls investigated here and also furans (*13*). The rate coefficient for 5-methyl-3*H*-furan-2-one is approximately 40% higher than that for 3*H*-furan-2-one and can be attributed to the positive inductive effect of the methyl group.

**Photochemistry of Unsaturated Carbonyls.** The photolytic behavior of the unsaturated 1,4-dicarbonyls butenedial, 4-oxo-2-pentenal, and 3-hexene-2,5-dione using both the super actinic lamps (VIS) and mercury lamps (UV) for conditions of 1000 mbar of synthetic air are summarized schematically in Figure 5. Apart from *trans*-3-hexene-2,5-dione, whose infrared absorption coefficients are known (*8*), quantification of the absolute yields of the photolysis products has not been possible since the concentrations of the carbonyls are not accurately known due to the presence of impurities. The results do, however, allow a distinction to be made between relatively major and minor products since calibrated IR spectra were available for many of the products. Such a gross categorization is given in Table 2. The measured first-order loss rates for the compounds using both the VIS and UV lamps are also listed in Table 2. Since the wall losses of the compounds were negligible, these values represent, to a first approximation, the photolysis frequencies of the compounds under the experimental conditions.

(*A*) *VIS Lamps*. No photolysis of maleic anhydride, 3*H*-furan-2-one, and 5-methyl-3*H*-furan-2-one was observed with the VIS lamps. Irradiation with the VIS lamps

**Table 2. Products Observed in Photolysis of Unsaturated Dicarbonyls Using UV ($\lambda$ = 254 nm) and VIS Lamps (320 ≤ $\lambda$ ≤ 480 nm, $\lambda_{max}$ = 360 nm)[a]**

| compound | VIS lamps |  |  | UV lamps |  |  |
|---|---|---|---|---|---|---|
|  |  | $k$ ($10^{-4}$ s$^{-1}$) | products |  | $k$ ($10^{-4}$ s$^{-1}$) | products |
| *cis/trans*-butenedial<br>(CHOCH=CHCHO) | cis | 2.6 ± 0.2 | major: 3*H*-furan-2-one | cis | 5.8 ± 0.2 | major: maleic anhydride, 3*H*-furan-2-one |
|  | trans | 1.4 ± 0.4 | minor: maleic anhydride (cis/trans isomerization accounts for ~45% of the decay) | trans | 3.9 ± 0.3 | minor: ethyne (cis/trans isomerization accounts for ≤40% of the decay) |
| *cis/trans*-4-oxo-2-pentenal<br>($CH_3COCH=CHCHO$) | cis/trans | 1.90 ± 0.10 | major: maleic anhydride, 5-methyl-3*H*-furan-2-one, HCHO, $CH_3OH$, $CH_3OOH$ (cis/trans isomerization accounts for ~20–30% of the decay) | cis/trans | 3.7 ± 0.2 | major: maleic anhydride, HCHO, $CH_3OH$, $CH_3OOH$<br>minor: 5-methyl-3*H*-furan-2-one, ethyne (cis/trans isomerization accounts for ≤20% of the decay) |
| *trans*-3-hexene-2,5-dione<br>($CH_3COCH=CHCOCH_3$) | cis | nd | cis isomer (only trans/cis isomerization is initially observed, no evidence for photodissociation) | cis | ~8.3 | cis isomer (30.3) |
|  | trans | 1.2 ± 0.1 |  | trans | 8.1 ± 0.9 | maleic anhydride (11.2), HCHO (6.0), HCOOH (6.5), $CH_3OH$ (3.0), $CH_3OOH$ (2.8), $CH_3C(O)OH$ (6.6), $CH_3COHCO$ (8.0), ethyne (traces detected), 4-oxo-2-pentenal (traces detected) |
| maleic anhydride | no photolysis observed |  |  |  | 1.0 ± 0.2 | CO (23), ethyne (8), HCOOH (2) $R_2C=C=O$ (trace)<br>$CO_2$ is a major product, but quantification is difficult with the experimental setup; one major product is still unidentified |
| 3*H*-furan-2-one | no photolysis observed |  |  | photolysis negligible |  |  |
| 5-methyl-3*H*-furan-2-one | no photolysis observed |  |  |  | 7.4 ± 0.1 | major: CO, HCHO, HCOOH<br>minor: $CH_3OH$, ketene<br>$CO_2$ is a major product, but quantification is difficult with the experimental setup; one major product is still unidentified |

[a] Absolute yields (in % C in parentheses beside the product) have only been obtained for *trans*-3-hexene-2,5-dione and maleic anhydride; all other results are only qualitative since the initial concentrations of the carbonyls could not be accurately determined and also in some cases products from impurities complicated a correct interpretation of the product spectra. The first-order rate losses $k$ of the compounds determined in the absence of the OH radical source are listed; since wall losses were negligible, these values correspond approximately to the photolysis frequencies of these compounds for the irradiation conditions employed. The measured photolysis frequencies for $NO_2$ in the reactor using the VIS and UV lamps were (1.2 ± 0.1) × $10^{-3}$ and (6.4 ± 0.3) × $10^{-4}$ s$^{-1}$, respectively. nd = not determined.

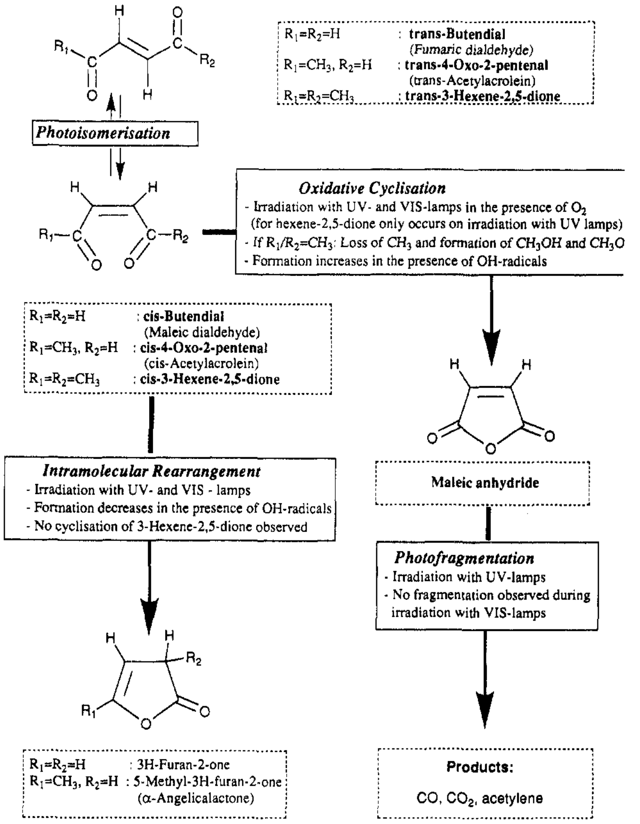


**Figure 5.** Schematic representation of the photochemical behavior of the 1,4-unsaturated carbonyls on irradiation with either the UV or VIS lamps in 1000 mbar of synthetic air. With UV irradiation, generally the oxidative cyclization pathway dominates. With the VIS lamps, the intramolecular rearrangement pathway dominates for butenedial while for 4-oxo-pentenal both intramolecular rearrangement and oxidative cyclization are important. The photolysis of 3-hexene-2,5-dione with the VIS lamps results mainly in photoisomerization.

causes photoisomerization of the trans to cis isomer and vice versa for butenedial, 4-oxo-2-pentenal, and 3-hexene-2,5-dione. For butenedial an [*trans*-butenedial]/[*cis*-butenedial] equilibrium ratio of approximately 0.46 ±0.05 was obtained under the irradiation conditions employed. For 4-oxo-2-pentenal, because of the poor spectral separation of the isomers, it has only been possible to make an estimation of the trans/cis equilibrium ratio. The measurements suggest that the equilibrium ratio lies within the range 0.4–0.6. For 3-hexene-2,5-dione, a value of 0.9 ± 0.2 has been obtained for the trans/cis equilibrium ratio under the present irradiation conditions. This is higher than the value of 0.45 ± 0.1 obtained in previous work in this laboratory in a different reactor (*9, 10*) and also the value of 0.55 ± 0.05 determined by Tuazon et al. (*8*). Photoisomerization accounts for ~45, ~30, and ≥90% of the observed photolysis rates for butenedial, 4-oxo-2-pentenal, and 3-hexene-2,5-dione, respectively.

Apart from trans/cis photoisomerization, irradiation of butenedial and 4-oxo-2-pentenal with the VIS lamps results in an intramolecular rearrangement which involves an 1,2-*H*-shift and leads to formation of 3*H*-furan-2-one and 5-methyl-3*H*-furan-2-one, respectively. In the case of 3-hexene-2,5-dione, such an intramolecular rearrangement is prevented by the second methyl group. A cis configuration is probably required for the intramolecular rearrangement, and Figure 6 shows a possible mechanism leading to furanone formation for *cis*-butenedial and *cis*-4-oxo-2-pentenal.

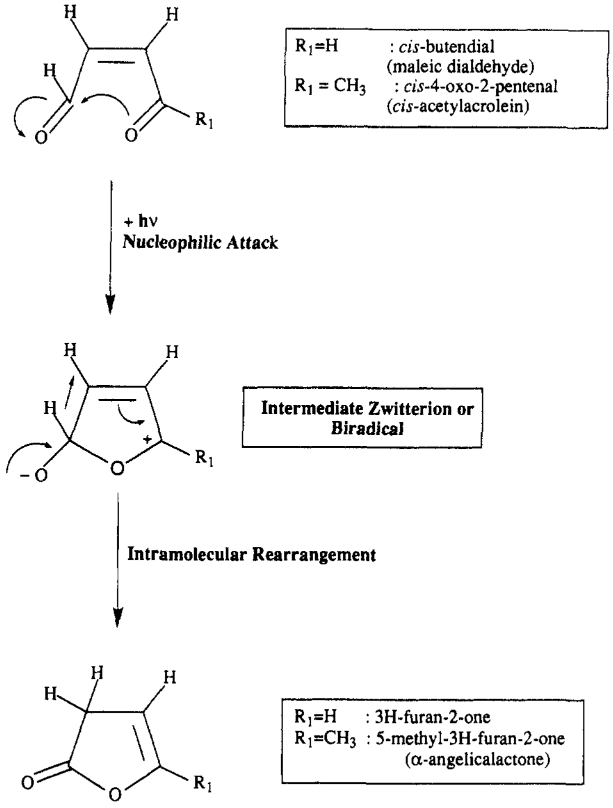


**Figure 6.** Possible mechanism for the photoinduced intramolecular rearrangement of butenedial and 4-oxo-2-pentenal to form 3*H*-furan-2-one and 5-methyl-3*H*-furan-2-one, respectively.

Irradiation with the VIS lamps also leads to an oxidative cyclization process and the formation of maleic anhydride for butenedial and 4-oxo-2-pentenal. Maleic anhydride or, indeed, other products were not observed in the VIS photolysis of *trans*-3-hexene-2,5-dione, indicating that it does not undergo photodissociation under the present irradiation conditions. The formation of maleic anhydride requires oxygen in the system; in experiments performed in 1000 mbar of $N_2$, the yield of maleic anhydride was negligible and furanone formation dominated. The formation of maleic anhydride also requires that butenedial loses both aldehydic hydrogens and that 4-oxo-2-pentenal loses an aldehydic hydrogen and a methyl group. Formation of $CH_3OH$ and $CH_3OOH$ was observed during the irradiation of *cis*/*trans*-4-oxo-2-pentenal. The observation of these compounds is a strong indication that $CH_3$ radicals are being produced during the photolysis since it is well-established that the reactions of $CH_3$ radicals in air can lead to $CH_3OH$ and $CH_3OOH$ by this sequence of reactions:

$$CH_3 + O_2 + M \rightarrow CH_3OO + M$$

$$CH_3OO + CH_3OO \rightarrow CH_3OH + HCHO + O_2$$

$$\rightarrow CH_3O + CH_3O + O_2$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2$$

$$CH_3OO + HO_2 \rightarrow CH_3OOH + O_2$$

Figure 7 shows possible mechanisms for the formation of maleic anhydride from the VIS photolysis of the unsaturated dicarbonyls. Since *trans*-3-hexene-2,5-dione does not photodissociate on irradiation with the VIS lamps, it would appear that the aldehydic hydrogens of butenedial

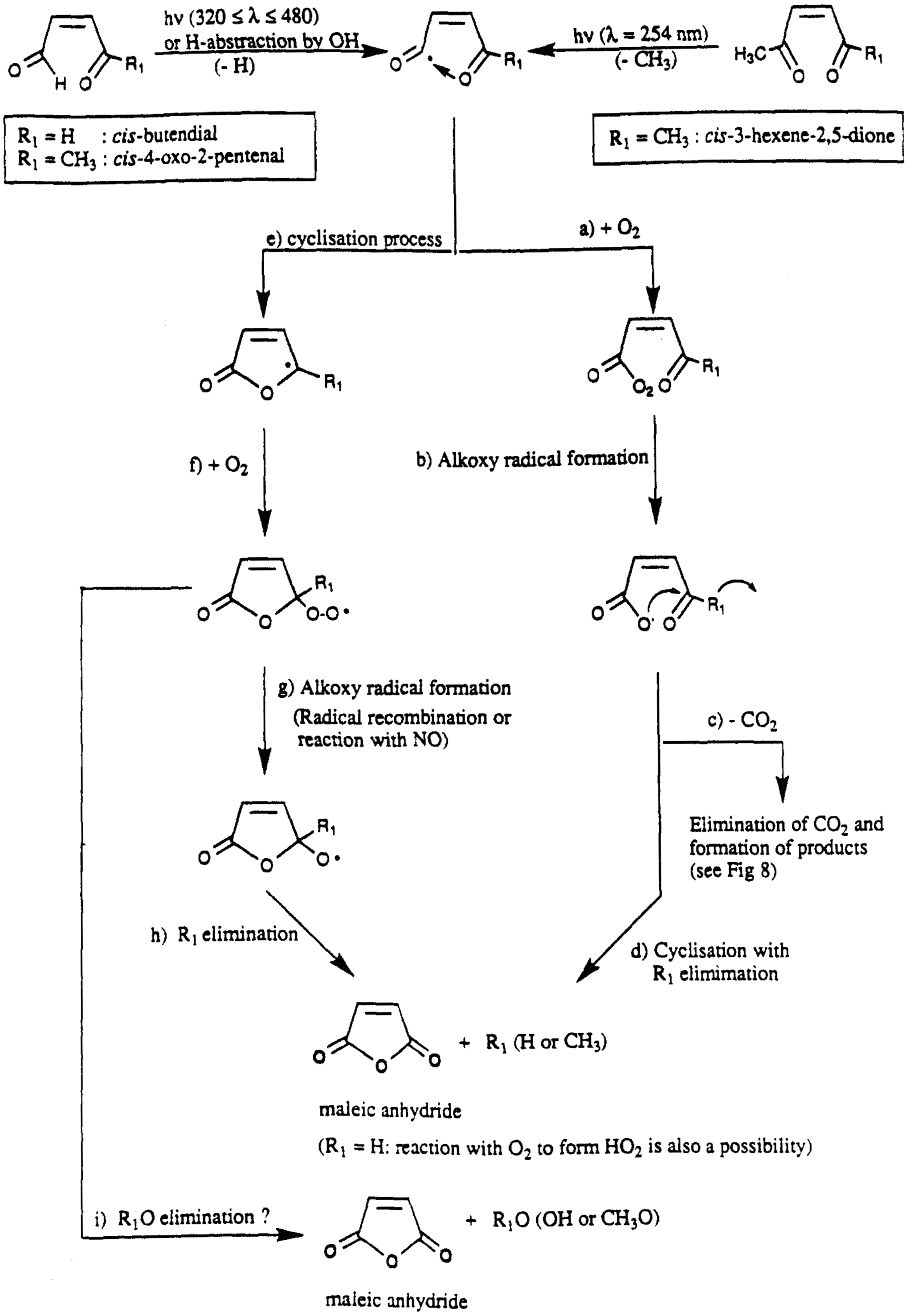


**Figure 7.** Possible mechanism for the formation of maleic anhydride in the UV and VIS photolysis of butenedial, 4-oxo-2-pentenal, and hexene-2,5-dione.

and 4-oxo-2-pentenal are photolytically fragmentated forming OCHCOCH=CHCO and $CH_3COCH$=CHCO radicals, respectively. The further reactions of these radicals resulting in the formation of maleic anhydride are unclear. These radicals can directly add $O_2$ to form a peroxy radical, which in the present system can recombine to form an alkoxy radical. The alkoxy radicals can either eliminate $CO_2$ and form other products or cyclize and eliminate the side group. These processes are represented by steps a–d in Figure 7. However, the radicals could also first cyclize and then add $O_2$. According to the current literature (*30, 31*), the resulting cyclic peroxy radicals from the latter process can, under the present experimental conditions, undergo recombination reactions forming cyclic alkoxy radicals. The cyclic alkoxy are expected to thermally decompose (*32*) with the ejection of either an H atom or a $CH_3$ radical and the formation of maleic anhydride. Evidence for an H ejection mechanism has recently been found for the thermal dissociation of the radicals $HOCH_2O$ (*33*) and $CH_3OCH_2O$ (*34, 35*), and it has also been established that the $\alpha$-alkoxy radicals formed in the degradation of diethyl ether and ethyl *tert*-butyl ether predominantly eject a $CH_3$ group in preference to reaction with $O_2$. In the case of OCHCOCH=CHCO, direct reaction of the radical with $O_2$ to form $HO_2$ and maleic anhydride is also a possibility. However, under the present experimental conditions, this is equivalent to an H atom ejection mechanism since the fate of the H atom is reaction with $O_2$ to produce $HO_2$. The above processes are represented by steps e–h in Figure 7. Alternately, the cyclic peroxy radicals formed in step g could eject either OH or $CH_3O$ and form maleic anhydride directly (Figure 7, step i). There is, however, no evidence in the literature for such a pathway for cyclic peroxy radicals. The observation of $CH_3OH$ and $CH_3OOH$ as products in the photolysis of 4-oxo-2-pentenal suggests that elimination of the $CH_3$ dominates.

Although quantification of the yields is difficult, the IR spectral evidence suggests that with the VIS lamps the formation of a furanone over maleic anhydride dominates for butenedial while for 4-oxo-2-pentenal the formation of both compounds is important.

(*B*) *UV Lamps.* With the UV lamps, photolysis was observed for butenedial, 4-oxo-2-pentenal, hexene-2,5-dione, and also maleic anhydride. Trans/cis isomerization was again observed, but photodissociation was the dominant process. Photodissociation accounted for approximately 60, 80, and 70% of the measured loss rates of butenedial, 4-oxo-2-pentenal, and hexene-2,5-dione, respectively. Irradiation of mixtures of the cis/trans isomers of butenedial and 4-oxo-2-pentenal with the UV lamps results in a significant increase of the yield of maleic anhydride compared to that obtained with the VIS lamps; a corresponding decrease in the yield of furanone formation was observed for butenedial and 4-oxo-2-pentenal. For 4-oxo-2-pentenal, a corresponding increase in the yields of HCHO, $CH_3OH$, and $CH_3OOH$ compared to the VIS system was also observed. The UV photolysis of *trans*-3-hexene-2,5-dione also results in the formation of maleic anhydride, HCHO, $CH_3OH$, and $CH_3OOH$. Other products formed include formic and acetic acids, glyoxal and methylgloxal, and low yields of 4-oxo-2-pentenal and ethyne. The enhancement of the yields of maleic anhydride, $CH_3OH$, and $CH_3OOH$ for butenedial and 4-oxo-2-pentenal on using the UV compared to the VIS lamps supports the assumption of bond fission before the cyclization can occur (Figure 7). Since maleic anhydride is also observed in the UV photolysis of *trans*-3-hexene-2,5-dione, the energy is obviously sufficient to rupture both the -CO-H and -CO-$CH_3$ bonds.

Interestingly, in the case of *trans*-3-hexene-2,5-dione, the measured $CH_3OH$ and HCHO yields when used to calculate a branching ratio $\alpha$ for the radical-producing channel in the recombination of $CH_3OO$ radicals results in a value ~0.29, which is at the lower end of the range of $\alpha$ values reported in literature, 0.23–0.43 (*1, 30, 31*). This suggests that the further reactions of $CH_3$ produced either directly by UV photolysis of 4-oxo-2-pental and *trans*-3-hexene-2,5-dione or in subsequent reactions of the resulting radicals are likely the major source of $CH_3OH$, HCHO, and $CH_3OOH$ in the photolysis systems.

The detection of 4-oxo-2-pentenal in the UV irradiation of *trans*-3-hexene-2,5-dione provides further evidence that a methyl group is eliminated from this compound. The resulting acetylacrylyl radical can be expected to be relatively long-lived due to resonance stabilization, and it is therefore possible that it can exist long enough to abstract an H atom from other hydrocarbons or perhaps $HO_2$ radicals, thus forming 4-oxo-2-pentenal:

$$CH_3COCH{=}CHCOCH_3 + h\nu\ (320 \geq \lambda \geq 480\ \text{nm}) \rightarrow CH_3COCH{=}CHCO + CH_3$$

$$CH_3COCH{=}CHCO + RH\ (HO_2) \rightarrow CH_3COCH{=}CHCHO + R(O_2)$$

Formation of methylglyoxal has also been observed in the photolysis of hexene-2,5-dione, and this can be expected to result from reactions of the acetylacrylyl radicals other than cyclization to form maleic anhydride, i.e., reaction with $O_2$:

$$CH_3COCH{=}CHCO + O_2 \rightarrow CH_3COCH{=}CHCOO_2$$

$$CH_3COCH{=}CHCOO_2 - \text{(several steps)} \rightarrow CH_3COCOCHO + \text{other products}$$

Formation of small yields of glyoxal and methylglyoxal has also been observed in the photolysis of butenedial and 4-oxo-2-pentenal, respectively. It is, however, presently not clear how much of this can be attributed to the photolysis of these compounds since control experiments have shown that the photolysis of the synthesis solvents, 2,5-dimethyl-2,5-dihydrofuran and 2,5-dimethoxy-2-methyl-5-dihydrofuran, which are present as impurities, can also result in the formation of glyoxal and methylglyoxal. Low yields of ethyne are also observed in the UV photolysis of the dicarbonyls. The ethyne is, however, a product of the UV photolysis of maleic anhydride as discussed however. As mentioned above, photolysis of maleic anhydride with the VIS lamps was negligible; however, irradiation with the UV lamps resulted in slow photodissociation and formation of ethyne, CO, $CO_2$, and HCOOH.

**Products from Reaction of OH Radicals with Unsaturated Carbonyls.** The products observed in the OH-initiated photooxidation of the unsaturated carbonyls using the 254-nm photolysis of $H_2O_2$ as the OH source are shown in Table 3. For butenedial, 4-oxo-2-pentenal, and 3-hexene-2,5-dione, 90% or more of the observed decay can be attributed to reaction with OH radicals; the remainer being cis/trans isomerization. For butenedial and 4-oxo-2-pentenal, the reaction with OH can proceed either by addition to the double bond or abstraction from the CHO group; whereas for 3-hexene-2,5-dione, the reaction will proceed mainly by OH addition to the double bond. The yields of maleic anhydride for butenedial and 4-oxo-2-pentenal have been estimated by assuming that the absorption coefficients for the carbonyl groups of these compounds are similar to these determined in this laboratory for acrolein ($CH_2{=}CHCHO$), methacrolein ($CH_2C{=}C(CH_3)CHO$), and crotonaldehyde ($CH_3CH{=}CH$-$CHO$). The estimations are probably reliable to within ±30%.

In the case of butenedial, a significant increase in the yield of maleic anhydride over that for the pure photolysis systems is observed, and the furanone formation becomes insignificant. Since reaction with OH dominates in the system, the result indicates that probably slightly less than 50% of the reaction proceeds by H atom abstraction from the aldehyde functional groups of butenedial. For 4-oxo-2-pentenal, a yield of only 40% has been estimated for maleic anhydride, suggesting that here the abstraction pathway also plays a very important role. These results can be compared with those reported in the literature for OH oxidation of the $\alpha,\beta$-unsaturated carbonyls acrolein,

**Table 3. Summary of Product Information Obtained in OH-Initiated Oxidation of Unsaturated Dicarbonyls in 1000 mbar of Total Pressure of Synthetic Air at 296 ± 2 K**[a]

| compound | OH radical source | products |
|---|---|---|
| mixture of *cis/trans*-butenedial isomers (CHOCH=CHCHO) | $H_2O_2 + h\nu$ | maleic anhydride (*50*), 3*H*-furan-2-one (*4*); glyoxal (expected major product of the OH addition reaction, yields are unknown due to formation of the compound from oxidation of impurities in the system); ≥90% of the reaction is due to reaction with OH |
| mixture of *cis/trans*-4-oxo-2-pentenal isomers (CH$_3$COCH=CHCHO) | $H_2O_2 + h\nu$ | maleic anhydride (*40*), 5-methyl-3*H*-furanone (*1*); methylglyoxal and glyoxal (expected major products of the OH addition reaction, yields are unknown due to formation of the compounds from oxidation of impurities in the system); ≥90% of the reaction is due to reaction with OH |
| *trans*-3-hexene-2,5-dione (CH$_3$COCH=CHCOCH$_3$) | $H_2O_2 + h\nu$ | HCHO (2.8), HCOOH (5.8), $CH_3OH$ (0.7), $CH_3OOH$ (4.3), methylglyoxal (19), maleic anhydride (1.1), cis isomer (8); ~90% of the decay can be attributed to reaction with OH; the carbon balance is ~42% C; a product is observed with spectral features similar to biacetyl ($CH_3COCOCH_3$), this may possibly be $CH_3COCH(OH)COCOCH_3$ or $HOCH_2COCH(OH)COCOCH_3$ |
|  | $CH_3ONO + h\nu$ | methyglyoxal (25), PAN (4.4), cis isomer (22); 70–80% of the decay can be attributed to reaction with OH; the carbon balance is ~50% C; HCHO and HCOOH are observed, but since they are also formed in the photolysis of CH$_3$ONO, yields for the OH + $CH_3COCH{=}CHCOCH_3$ reaction cannot be given |
| maleic anhydride | $CH_3ONO + h\nu$ | CO (20), HCOOH (3); $CO_2$ was also observed, but quantitization was not possible due to background $CO_2$; product investigations using the photolysis of $H_2O_2$ as the OH source give similar results; the major product of the OH reaction has not been identified, possible products are OHC-CO-O-CO-CHO and/or OC-CH(OH)-CO-CO<br>└——O——┘ |
| 3*H*-furan-2-one |  | no product information available |
| 5-methyl-3*H*-furan-2-one | $CH_3ONO + h\nu$ | CO, HCHO, HCOOH, $CH_3COOH$, $CH_3COCH$, and maleic anhydride are all minor products, and together account for ~10% C; $CO_2$ was observed, but quantitization was not possible due to background $CO_2$; product investigations using the photolysis of $H_2O_2$ as the OH source give similar results; the major products arising from the OH reaction still have to be identified; the residual product spectrum shows strong carbonyl absorptions which may be possibly due to OHC-O-CO-CH(CH$_3$)-CHO and/or HOCH-CO-CH(CH$_3$)-CO<br>└——O——┘ |

[a] The numbers in parentheses represent the yields of the compounds in % carbon; figures in italics are estimated yields as described in the text. The given yields have not been corrected for possible further reaction of the products, i.e., photolysis or reaction with OH radicals.

crotonaldehyde, and methacrolein (*20*) where H atom abstraction appears to be the major pathway for acrolein, while for crotonaldehyde and methacrolein both addition and abstraction pathways are of approximately equal importance.

Glyoxal has been observed as a product of the reaction of OH with butenedial, and glyoxal and methylglyoxal have been observed as products of the OH reaction with 4-oxo-2-pentenal. These are the expected products from the addition of OH to the double bond. Figure 8 gives a possible mechanism for the OH-initiated atmospheric oxidation of 1,4-unsaturated carbonyls using 4-oxo-2-pentenal as an example in which the pathways leading to glyoxal and methylglyoxal are indicated. Unfortunately, yields for glyoxal and methylglyoxal cannot be given for the OH-initiated oxidation of butenedial and 4-oxo-2-pentenal since these compounds are also products of the reaction of OH with the synthesis solvents also present in the reaction systems.

For *trans*-3-hexene-2,5-dione, product analyses have been performed using both the photolysis of $H_2O_2$/air and $CH_3ONO$/NO/air as the OH sources, and carbon balance, of ~42 and ~50% have been obtained, respectively. A typical product spectrum for the OH-initiated oxidation of *trans*-3-hexene-2,5-dione using the photolysis of $H_2O_2$ as the radical source is shown in Figure 9a. In both systems methylglyoxal is found to be a major product representing 19 and 25% carbon in the $H_2O_2$ and $CH_3ONO$ systems, respectively. The inset in Figure 9a shows the region 3500–2000 cm$^{-1}$ in which the formation of methylglyoxal can be clearly seen. The yields are based on the measured decay of the trans isomer and have not been corrected for isomerization of the trans to the cis isomer or loss due to photolysis and reaction with OH radicals.

When the above factors are taken into account in the system using $CH_3ONO$/NO/air as the OH source, a yield of ~30% C is calculated for methylglyoxal, i.e., the true yield of methylglyoxal from the OH reaction with hexene-2,5-dione. This yield is in good agreement with the value of 32% C reported previously from this laboratory on a product study of the OH + *trans*-3-hexene-2,5-dione reaction (*9, 10*) in which the thermal decay of peroxy nitric acid ($HO_2NO_2$) in the presence of NO was used as a "dark" OH radical source, thus excluding trans/cis isomerization. Tuazon et al. (*8*) have reported that they were unable to observe methylglyoxal above their detection limit (~6 × 10$^{12}$ molecule cm$^{-3}$) in kinetic and product studies of the OH reaction with *trans*-3-hexene-2,5-dione using the photolysis of $CH_3ONO$ as the OH radical source. The yields of methylglyoxal observed in the present studies suggest that methylglyoxal should have been detectable in the work of Tuzazon et al. (*8*). In the $NO_x$-containing system, the following sequence of reactions probably led to the formation of methylglyoxal:

(i) addition of OH and then $O_2$ to form hydroxyperoxy radicals:

$$CH_3CO\text{-}CH{=}CH\text{-}COCH_3 + OH \rightarrow CH_3CO\text{-}CH\text{-}CH(OH)\text{-}COCH_3$$

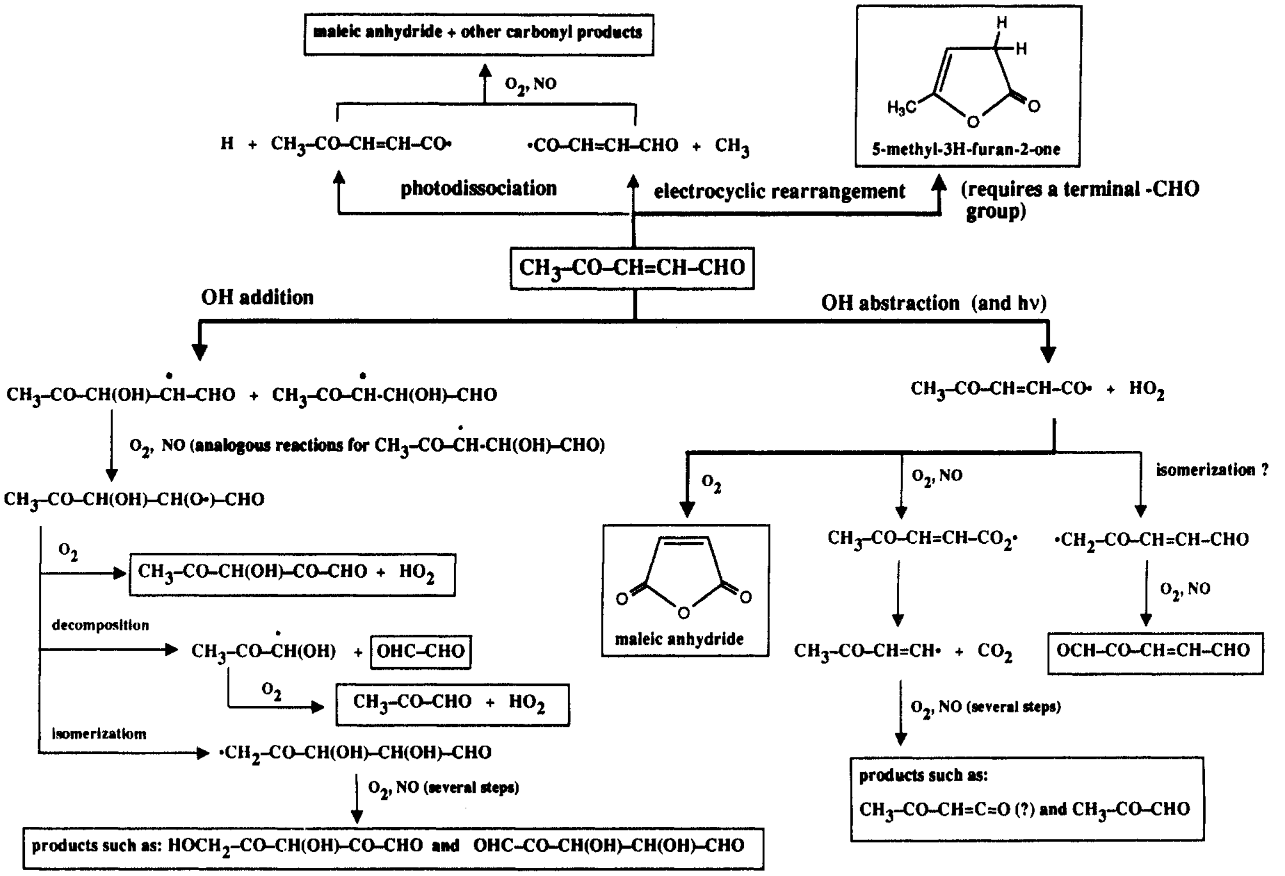


**Figure 8.** Possible mechanism for the OH-initiated atmospheric oxidation of 1,4-unsaturated carbonyls taking 4-oxo-2-pentenal as an example.

$$\mathrm{CH_3CO\text{-}CH\text{-}CH(OH)\text{-}COCH_3 + O_2 \rightarrow CH_3CO\text{-}CH(O_2)\text{-}CH(OH)\text{-}COCH_3}$$

(ii) conversion of the hydroxyperoxy to hydroxyalkoxy radicals by reaction with NO:

$$\mathrm{CH_3CO\text{-}CH(O_2)\text{-}CH(OH)\text{-}COCH_3 + NO \rightarrow CH_3CO\text{-}CH(O)\text{-}CH(OH)\text{-}COCH_3 + NO_2}$$

(iii) further reactions of the hydroxyalkoxy radicals to products:

$$\mathrm{CH_3CO\text{-}CH(O)\text{-}CH(OH)\text{-}COCH_3 \rightarrow CH_3COCHO + CH_3COCH(OH)\ (30\%)}$$

$$\mathrm{CH_3CO\text{-}CH(O)\text{-}CH(OH)\text{-}COCH_3 \rightarrow\rightarrow other\ products\ (70\%)}$$

$$\mathrm{CH_3COCH(OH) + O_2 \rightarrow CH_3COCHO + HO_2}$$

Since methylglyoxal accounts for ~30% C in the reaction system, the present results imply that the hydroxyalkoxy radicals must be decomposing at least 30% of the time, forming methylglyoxal. This is based on the assumption that the reaction of NO with the hydroxyperoxy radicals results fully in their conversion to hydroxyalkoxy radicals. The other 70% of the hydroxyalkoxy radicals must be reacting to form other products, two possibilities are (i) reaction with $O_2$ to form acetylformoin (hexane-2,3,5-trion-4-ol)

$$\mathrm{CH_3CO\text{-}CH(O^\bullet)\text{-}CH(OH)\text{-}COCH_3 + O_2 \rightarrow CH_3CO\text{-}CO\text{-}CH(OH)\text{-}COCH_3}$$

(ii) isomerization

$$\mathrm{CH_3CO\text{-}CH(O^\bullet)\text{-}CH(OH)\text{-}COCH_3 \rightarrow {}^\bullet CH_2CO\text{-}CH(OH)\text{-}CH(OH)\text{-}COCH_3}$$

$$\mathrm{CH_2CO\text{-}CH(OH)\text{-}CH(OH)\text{-}COCH_3 \rightarrow\rightarrow products\ such\ as\ HOCH_2CO\text{-}CH(OH)\text{-}CO\text{-}COCH_3}$$

These possibilities will be discussed below.

For the system using $H_2O_2$/air as the OH source, corrections to the methylglyoxal yield for loss due to photolysis and reaction with OH radicals are very minor and result in a value of ~21% C, which is considerably lower than the yield obtained in the $CH_3ONO$/NO system. In the $H_2O_2$ system, recombination reactions of the hydroxyperoxy radicals will presumably replace reaction with NO. Two major channels are expected to occur: one leading to the formation of hydroxyalkoxy radicals and the other to the formation of the products acetylformoin and hexane-2,5-dione-3,4-diol:

$$\mathrm{2CH_3CO\text{-}CH(O_2)\text{-}CH(OH)\text{-}COCH_3 \xrightarrow{k_a} 2CH_3CO\text{-}CH(O^\bullet)\text{-}CH(OH)\text{-}COCH_3 + O_2\ (65\text{–}70\%)}$$

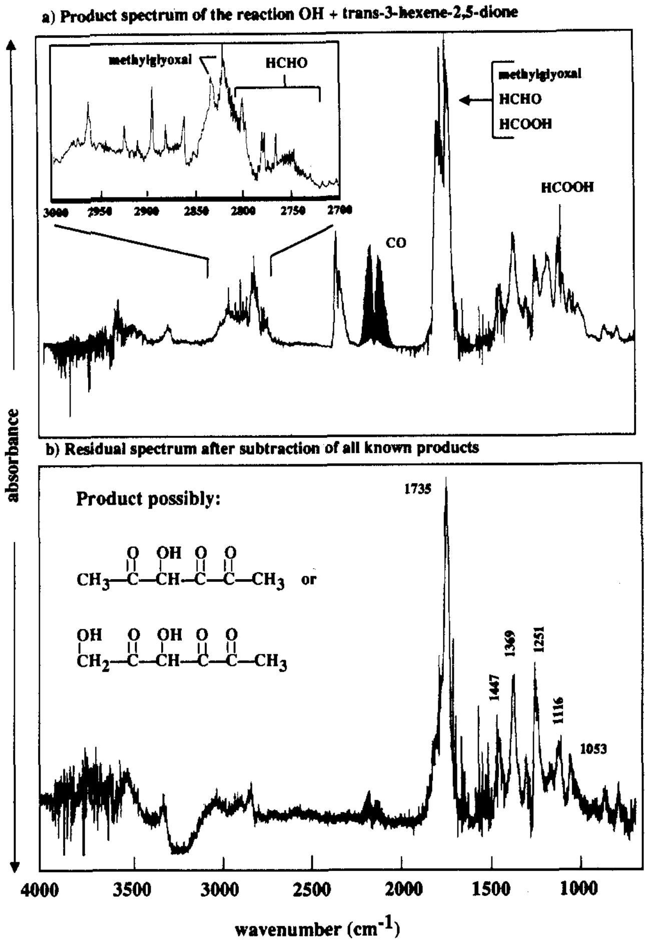


**Figure 9.** Infrared spectra in the range 4000–600 cm$^{-1}$: (a) product spectrum of a *trans*-3-hexene-2,5-dione/$H_2O_2$/air reaction mixture after 15 min of irradiation with the UV lamps; (b) residual spectrum after subtraction of the absorptions from all identified products.

$$\xrightarrow{-k_b} CH_3COCH(OH)\text{-}CH(OH)\text{-}COCH_3 + O_2 + CH_3CO\text{-}CO\text{-}CH(OH)\text{-}COCH_3 \; (30\text{–}35\%)$$

Only the radical-producing channel can result directly in the formation of methylglyoxal. If it is assumed that the thermal decomposition channel for the hydroxyalkoxy radicals occurs only 30% of the time as suggested by the results from the system using $CH_3NO/NO$ as the OH source, then an estimation can be made of the branching ratio for the hydroxyperoxy radical recombination reaction. To fit the observed 21% C yield, a branching ratio $\alpha$ $(=k_a/k_a + k_b)$ of 0.65–0.70 is required.

After subtraction of all the identified compounds (see Table 3) from the product spectra obtained using the photolysis of $H_2O_2$ as the OH source, the residual spectrum shown in Figure 9b is obtained. A similar residual spectrum is obtained for the $CH_3ONO/NO$/air system. Both residual spectra show a strong carbonyl absorption at around 1720 cm$^{-1}$. The identity of the compound(s) giving rise to these bands are not presently known, but the spectra have many similarities with that of biacetyl ($CH_3COCOCH_3$). It is thought that the residual spectrum may well be largely due to acetylformoin ($CH_3COCOCH(OH)COCH_3$), and attempts are currently underway in this laboratory to synthesize this compound.

Product analyses have been performed on the reactions of OH with maleic anhydride and 5-methyl-3*H*-furan-2-one, using both the photolysis of $H_2O_2$ and $CH_3ONO$/NO/air as the OH sources. The products of the reaction of OH with 3*H*-furan-2-one have not yet been investigated. For maleic anhydride, CO is a major product (20% C), and low yields of HCOOH (3% C) are observed using both light sources. With the UV lamps, acetylene (5% C) is also a product. $CO_2$ is apparently also a major product, but because of fluctuations in the background $CO_2$ concentration in the FTIR spectrometer, determination of the yield of this product is not currently possible. The product spectra show two carbonyl absorptions in the region 1820–1720 cm$^{-1}$, the identity of the compounds giving rise to these bands is not presently known but from mechanistic considerations OHC-CO-O-CO-CHO and OC-CH(OH)-CO-CO are two possibilities. No evidence
└────O────┘
could be found for the formation of PAN or other peroxynitrate type compounds.

For 5-methyl-3*H*-furan-2-one, the identified products using the photolysis of $CH_3ONO$/NO/air as the OH source account for only 10–12% of the reacted carbon. The results using the photolysis of $H_2O_2$ as the Oh source are similar. The major identified products are CO and maleic anhydride with yields of 5 and 3% C, respectively; other very minor products each with a yield of ~1% C are HCHO, HCOOH, and $CH_3COCHO$. Again $CO_2$ is probably also a major product but could not be quantified. The product spectrum shows absorptions typical for a PAN-type compound, and absorption due to the presence of another carbonyl compounds is also evident. The identity of these compounds is not presently known, but judging from the strength of the absorption bands they are major products. Based on the reaction of OH radicals with other cycloalkenes, a probable candidate for the carbonyl compound is $CH_3$-CO-O-CO-$CH_2$CHO.

**Atmospheric Lifetimes of Unsaturated Dicarbonyls.** The results of the present study have been used in conjunction with other literature data to estimate the atmospheric lifetime of the unsaturated 1,4-dicarbonyls due to photolysis and reactions with OH, $NO_3$, and $O_3$. The estimated lifetimes for the various compounds are listed in Table 4. In calculating the lifetimes, the following ambient tropospheric concentrations of OH radicals, $NO_3$ radicals, and $O_3$ were used: OH, 12-h average concentration of $1.6 \times 10^6$ molecules cm$^{-3}$ (*36*, *37*); $NO_3$, first-order loss rates were calculated using a 12-h average nighttime $NO_3$ radical concentration of $5 \times 10^8$ molecules cm$^{-3}$ (20 ppt) (*38*); $O_3$, 24-h average concentration of $7 \times 10^{11}$ molecules cm$^{-3}$ (30 ppb) (*39*). With the exception of the rate coefficient for the reaction of OH with *cis*-hexene-2,5-dione, which is from Tuazon et al. (*8*) all other OH rate coefficients are from this work. No rate coefficients are available in the literature for the reactions of $NO_3$ with the compounds, and consequently best estimates have been made from structure–reactivity comparisons using data in refs 21–25. Only the rate coefficient for the reaction of *cis*/*trans*-hexene-2,5-dione with $O_3$ is available in the literature (*8*); as for $NO_3$, all other values are the authors' best estimates from structure–reactivity comparisons from data in refs 21–25. Where applicable, rough estimations have been made of the photolysis lifetimes of the carbonyls. The estimates have been obtained by adjusting the photolysis frequencies for the carbonyls measured in the reactor to atmospheric conditions by multiplication with the factor:

**Table 4. Comparison of Rate Coefficients $k$ (units, $cm^3$ $molecule^{-1}$ $s^{-1}$) for Reactions of Unsaturated Carbonyls with $O_3$ and $NO_3$ and OH Radicals at 296 K and Estimations of Tropospheric Lifetimes $\tau$ of Compounds[a]**

| | $O_3$[b] | | $NO_3$[c] | | OH[d] | | photolysis[e] |
|---|---|---|---|---|---|---|---|
| compound | $k_{O_3}$ | $\tau_{O_3}$ | $k_{NO_3}$ | $\tau_{NO_3}$ | $k_{OH}$ | $\tau_{OH}$ | $\tau_{photolysis}$ |
| cis-butenedial | $2 \times 10^{-18}$ | 8.3 day | $1 \times 10^{-14}$ | 2.3 day | $52.1 \times 10^{-12}$ | 3.4 h | ~10 min |
| trans-butenedial | $2 \times 10^{-18}$ | 8.3 day | $1 \times 10^{-14}$ | 2.3 day | $\geq 24.1 \times 10^{-12}$ | ≤7.1 h | ~19 min |
| cis/trans-4-oxo-2-pentenal | $2 \times 10^{-18}$ | 8.3 day | $1 \times 10^{-14}$ | 2.3 day | $55.8 \times 10^{-12}$ | 3.1 h | ~13 min |
| cis-3-hexene-2-5-dione | $1.8 \times 10^{-18}$ | 8.2 day | $3 \times 10^{-14}$ | 0.8 day | $69.0 \times 10^{-12}$ | 2.5 h | ~30 min[f] |
| trans-3-hexene-2,5-dione | $8.3 \times 10^{-18}$ | 2.0 day | $1 \times 10^{-14}$ | 2.3 day | $40.0 \times 10^{-12}$ | 4.3 h | ~21 min |
| maleic anhydride | $<10^{-23}$ | <3200 yr | $\leq 10^{-18}$ | ≤63 yr | $1.5 \times 10^{-12}$ | 4.5 day | negligible |
| 3-*furan*-2-one | $2 \times 10^{-17}$ | 19.8 h | $3 \times 10^{-13}$ | 1.9 h | $44.5 \times 10^{-12}$ | 3.9 h | negligible |
| 5-methyl-3*H*-furan-2-one | $8 \times 10^{-17}$ | 5.0 h | $1 \times 10^{-12}$ | 0.6 h | $69.0 \times 10^{-12}$ | 2.5 h | negligible |

[a] Where applicable estimations have also been made of the atmospheric noontime photolyic lifetimes $j$ of the compounds for clear sky conditions. [b] The $k$ values for cis/trans-hexene-2,5-dione are from Tuazon et al. (*8*); all other values are the authors' best estimates from structure–reactivity comparisons from data in refs 20–24. The first-order loss rates were calculated using a 24-h average $O_3$ concentration of $7 \times 10^{11}$ molecules $cm^{-3}$ (30 ppb) (*39*). [c] Rate coefficients are not available in the literature for the reactions of these compounds with $NO_3$. The given $k$ values represent best estimates from structure–reactivity comparisons from data in refs 21–25. The first-order loss rates were calculated using an 12-h average nighttime $NO_3$ radical concentration of $5 \times 10^8$ molecules $cm^{-3}$ (20 ppt) (*38*). [d] The $k$ values are from this study (Table 1). The first-order loss rates were calculated using a 12-h average OH radical concentration of $1.6 \times 10^6$ molecules $cm^{-3}$ (*36, 37*). [e] The photolysis frequencies are from this work and have been adjusted to atmospheric conditions, which correspond to a noontime photolysis frequency for $NO_2$ of (8–9) $\times 10^{-3}$ $s^{-1}$, see text (*40*). [f] Not determined in this study; value taken from Tuazon et al. (*8*).

$$f = \frac{J_{NO_2}\text{ (at noon)}}{J_{NO_2}\text{ (in the reactor)}}$$

A noontime $NO_2$ photolysis frequency of $8 \times 10^{-3}$ $s^{-1}$ was used for the calculations (*40*). The calculations in Table 4 imply that photolysis will be more important as a loss pathway for butenedial, 4-oxo-2-pentenal, and 3-hexene-2,5-dione than reaction with OH radicals. It should be borne in mind, however, that the photolysis frequencies are very rough estimates for noontime conditions and are thus subject to a large degree of error. This aside, it is thought that the photolysis loss pathway will dominate for butenedial and 4-oxo-2-pentenal since photolysis results not only in isomerization but also in extensive bond dissociation. For 3-hexene-2,5-dione, however, the photolysis results mainly only in photoisomerization. Consequently, as has been pointed out by Tuazon et al. (*8*), reaction with OH radicals will be competitive with photodissociation. Reaction with $NO_3$ radicals should be an effective nighttime sink for these compounds. For 3*H*-furan-2-one and 5-methyl-3*H*-furan-2-one, reactions with OH and $NO_3$ radicals will be the major losses processes for daytime and nighttime, respectively. Maleic anhydride is suprisingly unreactive, and reaction with OH radicals will be the major atmospheric removal process.

## *Conclusions*

The rate coefficients for the reactions of OH radicals with unsaturated 1,4-dicarbonyls and furanones have all been found to be fast and of a magnitude consistent with their molecular structure. The only exception is for maleic anhydride where the cyclic anhydride function group reduces the rate coefficiently by up to a factor of 50 as compared to the other dicarbonyls. It has also been observed that the compounds butenedial, 4-oxo-2-pentenal, and 3-hexene-2,5-dione undergo photochemistry. Apart from cis/trans isomerization, it has been shown that oxidative cyclization to form maleic anhydride and an intramolecular rearrangement to form a furanone can occur; the relative importance of the respective pathways being dependent on the wavelength of the irradiation source. The observed photochemistry proves the previous postulation of Bandow et al. (*4*) that unsaturated dicarbonyls can undergo cyclization with the formation of acid anhydrides.

As mentioned in the Introduction, unsaturated dicarbonyl compounds have been detected in aromatic photooxidation systems, but in most cases the quantitative determination of their yields has not been possible. The present study shows that this, is in part, due to the high reactivity of the straight-chain unsaturated dicarbonyls compared to the parent aromatic compound. However, the present work shows that maleic anhydride and furanones are "unique" products of the photooxidation of the straight-chain unsaturated dicarbonyls. Since emission of these compounds to the atmosphere from other sources appears to be minor, in situ formation due to the photooxidation of aromatics probably represents the major atmospheric source of these compounds. Therefore, the possibility arises that these compounds could be used as "molecular markers" of the extent of transformation of aromatics in tropospheric air parcels. This would be particularly true for maleic anhydride due to its low reactivity toward oxidation with OH radicals. Obviously before the feasibility of such ideas can be assessed, much more experimental work is necessary concerning the synthesis and atmospheric chemistry of unsaturated dicarbonyls and also their yields in aromatic oxidation systems.

## *Literature Cited*

(1) Becker, K. H.; Barnes, I.; Bierbach, A.; Kirchner, F.; Thomas, W.; Wiesen, E.; Zabel, F. In *EUROTRAC Annual Reports, Part 8, LACTOZ*; Commission of the European Communities: Brussels, Belgium, 1991; pp 71–80 and 1992; pp 87–98.

(2) Barnes, I.; Becker, K. H.; Bierbach, A.; Wiesen, E. In *Laboratory Studies on Atmospheric Chemistry*; Air Pollution Research Report 42; Commission of the European Communities: Brussels, Belgium, 1991; pp 183–189.

(3) Identification of Hazardous Products Formed during Photochemical Transformation of Pollutants. Batelle Final Report to NSI Technology Services Corp. NSI P.O. No. 8806RG1852, 1989.

(4) Dumdei, B. E.; Kenny, D. V.; Shepson, P. B.; Kleindienst, T. E.; Nero, C. M.; Cupitt, L. T.; Claxton, L. D. *Environ. Sci. Technol.* **1988**, *22*, 1493.

(5) Gery, M. W.; Fox, D. L.; Kamens, R. M.; Stockburger, L. *Environ. Sci. Technol.* **1987**, *21*, 339.

(6) Bandow, H.; Washida, N.; Akimoto, H. *Bull Chem. Soc. Jpn.* **1985**, *58*, 2531.
(7) Bandow, H.; Washida, N. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2541.
(8) Tuazon, E. C.; Atkinson, R.; Carter, W. P. L. *Environ. Sci. Technol.* **1985**, *19*, 265.
(9) Klein, Th. Ph.D. Dissertation, Bergische Universität-Gesamthochschule Wuppertal, 1987.
(10) Becker, K. H.; Klein, Th. In *Proceedings of the 4th European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants*; Angeletti, G., Restelli, G., Eds.; Riedel: Dordrecht, Holland, 1987; pp 320–326.
(11) Knispel, R.; Koch, R.; Siese, M.; Zetzsch, C. *Ber. Bunsenges. Phys. Chem.* **1990**, *94*, 1375.
(12) Barnes, I.; Becker, K. H.; Mihalopoulos, N. *J. Atmos. Chem.*, in press.
(13) Bierbach, A.; Barnes, I.; Becker, K. H. *Atmos. Environ.* **1992**, *26A*, 813.
(14) Paulson, S. E.; Flagan, R. C.; Steinfeld, J. H. *Int. J. Chem. Kinet.* **1992**, *24*, 79.
(15) Hufford, D. L.; Tarbell, D. S.; Koszalka, T. R. *J. Am. Chem. Soc.* **1952**, *74*, 3014.
(16) Bierbach, A.; Barnes, I.; Becker, K. H. Bergische Universität-Gesamthochschule Wuppertal, Germany; paper in preparation, 1993.
(17) Wiesen, E.; Barnes, I.; Becker, K. H. Bergische Universität-Gesamthochschule, Wuppertal, Germany; unpublished results, 1993.
(18) Lepage, L.; Lepage, Y. *Synthesis* **1983**, 1018.
(19) Levisalles, J. *Bull. Soc. Chim. Fr.* **1957**, 997.
(20) Atkinson, R. *Atmos. Environ.* **1990**, 26A, 1.
(21) Grosjean, D.; Williams, E. L., II *Atmos. Environ.* **1992**, *26A*, 1395.
(22) Atkinson, R.; Carter, W. P. L. *Chem. Rev.* **1984**, *84*, 437.
(23) Atkinson, R. *Int. J. Chem. Kinet.* **1987**, *19*, 799.
(24) Sabljic, A.; Güsten, H. *Atmos. Environ.* **1990**, *24A*, 73.
(25) Wayne, R. P.; Barnes, I.; Biggs, P.; Burrows, J. P.; Canosa-Mas, C. E.; Hjorth, J.; LeBras, G.; Moortgat, G. K.; Perner, D.; Poulet, G.; Restelli, G.; Sidebottom, H. *Atmos. Environ.* **1991**, *25A*, 1.
(26) Tuazon, E. C.; Atkinson, R.; Aschmann, S. M.; Goodman, M. A.; Winer, A. M. *Int. J. Chem. Kinet.* **1988**, *20*, 241.
(27) Abbatt, J. P.; Anderson, J. G. *J. Phys. Chem.* **1991**, *95*, 2382.
(28) Grosjean, D. *J. Air Waste Manage Assoc.* **1990**, *40*, 1397.
(29) Grosjean, D. *J. Air Waste Manage Assoc.* **1990**, *40*, 1664.
(30) Wallington, T. J.; Dagaut, P.; Kurylo, M. J. *Chem. Rev.* **1992**, *92*, 667.
(31) Lightfoot, P. D.; Cox, R. A.; Crowley, J. N.; Destriau, M.; Hayman, G. D.; Jenkin, M. E.; Moortgat, G. K.; Zabel, F. *Atmos. Environ.* **1992**, *26A*, 1805.
(32) Atkinson, R.; Carter, W. P. L. *J. Atmos. Chem.* **1991**, *13*, 195.
(33) Veyret, B.; Roussel, P.; Lesclaux, R. *Int. J. Chem. Kinet.* **1984**, *16*, 1599.
(34) Jenkin, M. E.; Hayman, G. D. In *Chemical Mechanisms Describing Tropospheric Processes*; Air Pollution Research Report 45; Commission of the European Communities: Brussels, Belgium, 1992; pp 143–148.
(35) Wallington, T. J.; Japar, S. M. *Environ. Sci. Technol.* **1991**, *25*, 410.
(36) Prinn, R.; Cunnold, D.; Simmonds, P.; Alyea, F.; Boldi, R.; Crawford, A.; Fraser, P.; Gutzler, D.; Hartley, D.; Rosen, R.; Rasmussen, R. *J. Geophys. Res.* **1992**, *97*, 2445.
(37) Crutzen, P. J.; Zimmermann, P. H. *Tellus* **1991**, *43AB*, 136.
(38) Atkinson, R. *J. Phys. Chem. Ref. Data* **1991**, *20*, 459.
(39) Logan, J. A. *J. Geophys. Res.* **1985**, *90* (D6), 10463.
(40) Parrish, D. D.; Murphy, P. C.; Albritton, D. L.; Fehsenfeld, F. C. *Atmos. Environ.* **1983**, *17*, 1365.

*Received for review September 2, 1993. Revised manuscript received November 30, 1993. Accepted December 15, 1993.*®

---

® Abstract published in *Advance ACS Abstracts*, February 1, 1994.