Kinetics and Products of the Gas-Phase Reactions of 6-Methyl-5-hepten-2-one and trans-Cinnamaldehyde with OH and NO₃ Radicals and O₃ at 296 \pm 2 K

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6-Methyl-5-hepten-2-one is an atmospheric reaction product of the biogenic emission linalool, and trans-cinnamaldehyde is a model compound for dicarbonyls formed from the OH radical-initiated reaction of naphthalene. These carbonyl compounds react in the atmosphere, and photolysis and the gas-phase reactions of 6-methyl-5-hepten-2-one and transcinnamaldehyde with OH radicals, NO₃ radicals, and O_3 have been investigated at 296 \pm 2 K and atmospheric pressure of air. Using relative rate methods, the respective rate constants obtained for the OH radical, NO₃ radical, and O₃ reactions were (in cm³ molecule⁻¹ s⁻¹ units) as follows: for 6-methyl-5hepten-2-one: $(1.57 \pm 0.39) \times 10^{-10}$, $(7.5 \pm 3.0) \times 10^{-12}$, and $(3.9 \pm 1.5) \times 10^{-16}$; for *trans*-cinnamaldehyde: $(4.8 \pm 1.4) \times 10^{-11}$, $(1.9 \pm 0.7) \times 10^{-14}$, and (2.2 ± 10^{-14}) 1.8) \times 10⁻¹⁸. *trans*-Cinnamaldehyde was also observed to photolyze. Benzaldehyde was observed and quantified from the OH radical reaction with transcinnamaldehyde, with a yield of 0.90 \pm 0.39. Acetone and CH₃C(O)CH₂CH₂CHO were observed and guantified from the OH radical and O₃ reactions with 6-methyl-5-hepten-2-one, with formation yields of 0.706 ± 0.054 and 0.59 ± 0.13 , respectively, from the OH radical reaction and 0.302 \pm 0.048 and 0.82 \pm 0.21, respectively, from the O_3 reaction. The reaction mechanisms are discussed.

Introduction

A large number of organic compounds are emitted into the atmosphere from anthropogenic and biogenic sources (1).

In the atmosphere, gas-phase photooxidations of directly emitted volatile organic compounds lead to the formation of products, which are often carbonyl compounds more oxidized and less volatile than the directly-emitted precursor compounds (2). For a complete understanding of the atmospheric chemistry of an emitted compound, the subsequent atmospheric reactions of its reaction products also need to be known. In this work, we have investigated the atmospheric chemistry of 6-methyl-5-hepten-2-one [(CH₃)₂C=CHCH₂CH₂C(O)CH₃] and trans-cinnamaldehyde [trans-C₆H₅CH=CHCHO]. 6-Methyl-5-hepten-2-one is a product of the OH radical-initiated reaction of linalool [(CH₃)₂C=CHCH₂CH₂C(CH₃)(OH)CH=CH₂] (3), a terpene emitted from orange blossoms (4) and from certain pine trees in southern Europe (5), while trans-cinnamaldehyde is structurally related to commercially unavailable ringopened C₁₀-dicarbonyls formed in significant yield from the OH radical-initiated reaction of naphthalene (6). The kinetic and product data obtained for these two oxygenated compounds add significantly to the database concerning the atmospheric chemistry of products formed from the atmospheric photooxidations of volatile organic compounds of anthropogenic and biogenic origin.

Experimental Section

The experimental methods used were similar to those described previously (7, 8). All experiments were carried out at 296 ± 2 K and 740 Torr total pressure of purified air at ~5% relative humidity in a ~6700-L Teflon chamber equipped with two parallel banks of black lamps and with a Teflon-coated fan to ensure rapid mixing of reactants during their introduction.

Rate Constant Measurements. The rate constants for the OH radical, NO_3 radical, and O_3 reactions were measured using relative rate methods in which the relative disappearance rates of the carbonyl and a reference organic, whose reaction rate constant with OH radicals, NO_3 radicals, or O_3 is reliably known, were measured in the presence of OH radicals, NO_3 radicals, or O_3 (ϑ). Providing that the carbonyl and the reference organic reacted only with OH radicals, NO_3 radicals, or O_3 , then,

$$\ln \left\{ \frac{\left[\text{carbonyl} \right]_{t_0}}{\left[\text{carbonyl} \right]_t} \right\} - D_t = \frac{k_1}{k_2} \left\{ \ln \left[\frac{\left[\text{reference organic} \right]_{t_0}}{\left[\text{reference organic} \right]_t} \right] - D_t \right\}$$
(D)

where [carbonyl]_{t0} and [reference organic]_{t0} are the concentrations of the carbonyl and reference organic, respectively, at time t_0 ; [carbonyl]_t and [reference organic]_t are the corresponding concentrations at time t; D_t is a term to take into account any dilution caused by additions to the chamber during an experiment ($D_t = 0.0014 - 0.0028$ per addition); and k_1 and k_2 are the rate constants for reactions 1 and 2, respectively.

$$\begin{array}{c} OH\\ NO_{3}\\ O_{3} \end{array} \right\} + carbonyl \rightarrow products \qquad (1)$$

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TABLE 1

Rate Constant Ratios k_1/k_2 and Rate Constants k_1 for Gas-Phase Reactions of 6-Methyl-5-hepten-2-one and trans-Cinnamaldehyde with OH Radicals, NO₃ Radicals, and O₃ at 296 \pm 2 K and Atmospheric Pressure

carbonyl	ref compd	k_{1}/k_{2}^{a}	k_1 (cm ³ molecule ⁻¹ s ⁻¹)	
			experimental ^b	estimated ^c
	OH R	adical Reaction		
6-methyl-5-hepten-2-one	trans-2-butene	2.42 ± 0.35	$(1.57 \pm 0.39) imes 10^{-10}$	9.2×10^{-11}
trans-cinnamaldehyde	trans-2-butene	0.74 ± 0.14	$(4.8 \pm 1.4) \times 10^{-11}$	4.1×10^{-11}
	NO ₃ R	adical Reaction		
6-methyl-5-hepten-2-one	2-methyl-2-butene	0.80 ± 0.14	$(7.5 \pm 3.0) \times 10^{-12}$	9.4×10^{-12}
trans-cinnamaldehyde	propene	2.07 ± 0.18	$(1.9 \pm 0.7) \times 10^{-14}$	$5.1 imes 10^{-15} d$
	(D ₃ Reaction		
6-methyl-5-hepten-2-one	2-methyl-2-butene	0.98 ± 0.14	$(3.9 \pm 1.5) \times 10^{-16}$	4.0×10^{-16}
trans-cinnamaldehyde	propene	0.23 ± 0.18	$(2.2 \pm 1.8) \times 10^{-18}$	$9.0 imes 10^{-19} \ d$

^{*a*} Indicated errors are two least-squares standard deviations. ^{*b*} Placed on an absolute basis by use of rate constants k_2 (in cm³ molecule⁻¹ s⁻¹) at 296 K of k_2 (DH + *trans*-2-butene) = 6.48 × 10⁻¹¹ (±20%) (*2*, 17), k_2 (NO₃ + propene) = 9.24 × 10⁻¹⁵ (±35%) (*2*, 15), k_2 (NO₃ + 2-methyl-2-butene) = 9.37 × 10⁻¹² (±35%) (*2*, 15), k_2 (O₃ + propene) = 9.68 × 10⁻¹⁸ (±25%) (*2*), and k_2 (O₃ + 2-methyl-2-butene) = 3.96 × 10⁻¹⁶ (±35%) (*2*). ^{*c*} Estimated as described in refs 15, 16 and 18 unless noted otherwise. ^{*d*} Literature rate constants for the structurally related carbonyl crotonaldehyde [CH₃CH=CHCHO] (*2*); see text.

$$\begin{array}{c} OH\\ NO_{3}\\ O_{3} \end{array} \right\} + reference \ organic \rightarrow products \qquad (2)$$

Plots of $\{\ln([\operatorname{carbonyl}]_{t_0}/[\operatorname{carbonyl}]_t) - D_t\}$ against $\{\ln([\operatorname{reference organic}]_{t_0}/[\operatorname{reference organic}]_t) - D_t\}$ should therefore be straight lines with slope k_1/k_2 and zero intercept.

The initial concentrations of 6-methyl-5-hepten-2-one, *trans*-cinnamaldehyde, and the reference organic were $(1.9-2.5) \times 10^{13}$, $(0.64-1.3) \times 10^{13}$, and $\sim 4.8 \times 10^{13}$ molecule cm⁻³, respectively. The reference organics used in these relative rate measurement experiments are listed in Table 1.

Hydroxyl radicals were generated from the photolysis of 2.4×10^{14} molecule cm⁻³ of methyl nitrite (CH₃ONO) in air at wavelengths > 300 nm (9), and 2.4×10^{14} molecule cm⁻³ of NO was added to the reactant mixtures to suppress the formation of O_3 and hence of NO_3 radicals (9). Irradiations were carried out at 20% of the maximum light intensity, corresponding to an NO₂ photolysis rate of 1.5 $\times 10^{-3}$ s⁻¹, for 1–6 min. In addition, carbonyl–air mixtures with $(4.2-6.7) \times 10^{15}$ molecule cm⁻³ of cyclohexane to scavenge any OH radicals formed from residual NO_x or impurities in the chamber were irradiated at 20% of the maximum light intensity for up to 30 min to assess the importance of photolysis by the black lamps. Nitrate radicals were generated by the thermal decomposition of N_2O_5 (10) in the presence of (1.2–2.4) \times 10¹⁴ molecule cm⁻³ of NO₂. Three or four additions of N₂O₅ [each addition corresponding to an initial concentration of N2O5 in the chamber of $(0.5-5) \times 10^{13}$ molecule cm⁻³] were made to the chamber during an experiment. For the O₃ reactions, $(2.6-3.3) \times 10^{16}$ molecule cm⁻³ of cyclohexane was used (7, 8, 11) to scavenge >95% of the OH radicals formed from the reactions of O_3 with the reference organics (12) and the carbonyls. One to three additions of O₃ in O₂ diluent (each O_3/O_2 addition corresponding to an initial O_3 concentration in the chamber of ${\sim}5 \times 10^{12}$ molecule cm⁻³) were made to the chamber during an experiment.

The concentrations of the carbonyls and reference organics were measured during these experiments by gas chromatography with flame ionization detection (GC-FID). The reference organics propene, *trans*-2-butene, and

2-methyl-2-butene were analyzed as described previously (*12*). For the analyses of the carbonyls 6-methyl-5-hepten-2-one and *trans*-cinnamaldehyde, 100 cm³ volume gas samples were collected from the chamber onto Tenax-TA solid adsorbent with subsequent thermal desorption at \sim 225–250 °C onto a 30-m DB-5.625 or DB-5 megabore column, initially held at 0 (*trans*-cinnamaldehyde) or 40 °C (6-methyl-5-hepten-2-one) and then temperature programmed to 250 °C at 8 °C min⁻¹.

Product Studies. The products formed from the gasphase reactions of the OH radical with 6-methyl-5-hepten-2-one and *trans*-cinnamaldehyde in the presence of NO and from the reaction of O_3 with 6-methyl-5-hepten-2-one were investigated. These experiments were carried out as described above with similar initial reactant concentrations, except for the absence of the reference organic. As discussed in detail previously (*8, 12, 13*), the OH radical formation yield from the O_3 reaction with 6-methyl-5hepten-2-one was derived from the measured amounts of cyclohexanone and cyclohexanol formed from the reaction of OH radicals with cyclohexane.

Gas samples were collected from the chamber onto Tenax-TA solid adsorbent, with subsequent thermal desorption and analyses by GC-FID (as described above), combined gas chromatography-mass spectrometry (GC/ MS) with positive ion chemical ionization [using a 60-m HP-5 fused silica capillary column in a Hewlett Packard (HP) 5890 GC interfaced to a HP 5971 mass selective detector and HP G1072A CI detector, operated in the scanning mode], and gas chromatography with FTIR detection (GC-FTIR), using a 30-m DB-5MS capillary column in a HP 5890 GC interfaced to a HP 5965B FTIR detector. GC-FID response factors for the reactants and products were measured (6-methyl-5-hepten-2-one, acetone, and benzaldehyde) or estimated using the equivalent carbon number concept of Scanlon and Willis (14), as described previously (7, 8).

Chemicals. Acetone, benzaldehyde, *trans*-2-butene, *trans*-cinnamaldehyde, cyclohexane, 2-methyl-2-butene, 6-methyl-5-hepten-2-one, propene, and NO were all of \geq 98% purity. Methyl nitrite and N₂O₅ were prepared as described previously (*9*, *10*) and stored under vacuum at 77 K. NO₂ was prepared immediately prior to use by reacting NO with an excess of O₂, and O₃ was prepared as needed by a Welsbach T-408 ozone generator.



FIGURE 1. Plots of eq I for the gas-phase reactions of the OH radical with 6-methyl-5-hepten-2-one and *trans*-cinnamaldehyde, with *trans*-2-butene as the reference organic.

Results and Discussion

Photolysis and OH Radical, NO₃ Radical, and O₃ Reaction Rate Constants. No photolysis (<1%) of 6-methyl-5hepten-2-one was observed over a 30-min period at 20% of the maximum light intensity. In contrast, photolysis of *trans*-cinnamaldehyde at 20% of the maximum light intensity for 30 min led to the disappearance of 33% of the *trans*-cinnamaldehyde, with the appearance of a product tentatively identified by its infrared (IR) and MS spectra as *cis*-cinnamaldehyde. The photolysis rate of *trans*-cinnamaldehyde was $0.0129 \pm 0.0026 \text{ min}^{-1}$ (the indicated error is two least-squares standard deviations) under the light intensity and spectral conditions employed, and the amount of *cis*-cinnamaldehyde formed was 57 ± 7% of the *trans*cinnamaldehyde photolyzed (the indicated error is again two standard deviations).

Representative experimental data obtained from the kinetic experiments are plotted in accordance with eq I in Figure 1 for the OH radical reactions with 6-methyl-5hepten-2-one and trans-cinnamaldehyde. In all cases, good straight line plots were observed, and no effect of the initial NO₂ concentrations on the rate constant ratios k_1/k_2 were observed for the NO₃ radical reactions. The rate constant ratios k_1/k_2 obtained from least-squares analyses of the experimental data are given in Table 1. For the reaction of O_3 with *trans*-cinnamaldehyde, <19% of the initially present trans-cinnamaldehyde was consumed by reaction, and the rate constant ratio k_1/k_2 given in Table 1 is subject to significant uncertainties. The measured rate constant ratios k_1/k_2 are placed on an absolute basis as described in footnote b in Table 1, and the resulting rate constants k_1 are given in Table 1.

The reactions of 6-methyl-5-hepten-2-one with OH radicals, NO_3 radicals, and O_3 proceed totally (NO_3 radical and O_3 reactions) or mainly (OH radical reaction) by initial

addition to the >C=C< bond (2, 15–17), and the rate constants for the addition reactions are estimated to be the same as those for the corresponding reactions of 2-methyl-2-butene (2, 15, 16, 18). For the OH radical reaction with 6-methyl-5-hepten-2-one, H-atom abstraction from the various C–H bonds is estimated to be minor, accounting for ~5% of the overall OH radical reaction (2, 17, 18). The estimated rate constants for the reactions of OH radicals, NO₃ radicals, and O₃ with 6-methyl-5-hepten-2-one are also given in Table 1, and are within a factor of \leq 1.7 of our measured values.

The OH radical and NO3 radical reactions with transcinnamaldehyde can proceed by addition to the >C=C< bond, addition to the aromatic ring, and H-atom abstraction from the CHO group (2, 15, 18). Addition of OH radicals and NO₃ radicals to the aromatic ring is expected to be of minor (OH radical) or negligible (NO3 radical) importance (2, 15, 17, 18). The OH radical reaction rate constant for addition to the >C=C< bond can be estimated using the CHO group substituent factor (18), and the resulting calculated overall rate constant is given in Table 1. For the NO₃ radical and O₃ reactions, trans-cinnamaldehyde is expected to be of similar reactivity to crotonaldehyde [CH₃CH=CHCHO] (2, 15, 17), and the rate constants for the reactions of NO₃ radicals and O₃ with crotonaldehyde (2) are given in Table 1 and are within a factor of 4 of those we measured for trans-cinnamaldehyde.

Products of the OH Radical and O₃ Reactions. The products of the atmospherically important reactions of 6-methyl-5-hepten-2-one with OH radicals and O_3 and of *trans*-cinnamaldehyde with OH radicals were investigated.

6-Methyl-5-hepten-2-one. GC-FID, GC-MS, and GC-FTIR analyses of irradiated CH₃ONO-NO-6-methyl-5hepten-2-one-air mixtures and reacted O₃-6-methyl-5hepten-2-one-cyclohexane (in excess)-air mixtures showed the formation of acetone plus a second compound in both reactions. Additionally, cyclohexanone and cyclohexanol were observed in the O₃ reaction, indicating the formation of OH radicals (12, 13). The IR spectra of the second product from the OH radical and O3 reactions had absorption bands at 1164, 1367, 1740 (strong), 2721, 2817, and 2918 cm⁻¹. The absorption bands at 2721 and 2817 cm⁻¹ are attributed to the C-H stretch in a CHO group and that at 1740 cm⁻¹ to a C=O stretch. The methane-CI mass spectra had a base ion peak at 101 u (unified atom mass unit) and weaker ion peaks at 129 and 141 u. The 101 u ion peak is therefore the $[M + H]^+$ ion, and the product of the OH radical and O₃ reactions has a molecular weight of 100. These IR and MS data are consistent with the second product of both reactions being CH₃C(O)CH₂CH₂CHO, as expected from cleavage of the >C=C < bond (2).

Secondary reactions of the products with the OH radical occur in the OH radical reaction, and the measured concentrations of acetone and CH₃C(O)CH₂CH₂CHO were corrected to take into account their reactions with the OH radical (*19*) using measured or estimated rate constants for the OH radical reactions with acetone and CH₃C(O)CH₂-CH₂CHO of 2.15×10^{-13} cm³ molecule⁻¹ s⁻¹ at 296 K (*2*) and 2.63×10^{-11} cm³ molecule⁻¹ s⁻¹ (*18*), respectively. The corrections for secondary reactions were <1% for acetone and $\leq 12\%$ for CH₃C(O)CH₂CH₂CHO. Plots of the amounts of acetone and CH₃C(O)CH₂CH₂CHO formed, corrected for secondary reactions with the OH radical, against the amounts of 6-methyl-5-hepten-2-one reacted with the OH radical are shown in Figure 2, and plots of the amounts of







FIGURE 3. Plots of the amounts of acetone (\triangle), CH₃C(0)CH₂CH₂CH₀(\bigcirc), and cyclohexanone plus cyclohexanol (\bullet) formed against the amounts of 6-methyl-5-hepten-2-one reacted with 0₃ in the presence of sufficient cyclohexane to scavenge \geq 95% of the OH radicals formed.

acetone, $CH_3C(O)CH_2CH_2CHO$, and cyclohexanone plus cyclohexanol formed against the amounts of 6-methyl-5hepten-2-one reacted with O_3 are shown in Figure 3. Leastsquares analyses of the acetone and $CH_3C(O)CH_2CH_2CHO$ data lead to the formation yields given in Table 2.

A least-squares analysis of the amounts of cyclohexanone plus cyclohexanol formed against the amounts of 6-methyl-5-hepten-2-one reacted with O₃ in the presence of sufficient cyclohexane to scavenge \geq 95% of the OH radicals formed leads to a {([cyclohexanone] + [cyclohexanol])/([6-methyl-5-hepten-2-one] reacted)} ratio of 0.377 ± 0.058, where the indicated error is two least-squares standard deviations combined with estimated overall uncertainties in the GC-FID response factors for the reactants and products of ±5% each. A yield of 0.50 for the formation of cyclohexanone plus cyclohexanol from the OH radical reaction with cyclohexane in reacting O₃-alkene-air systems (*12*) is used to derive the OH radical formation yield given in Table 2.

TABLE 2



	reactio	reaction with		
product	ОН	O ₃ ^a		
6-Me	thyl-5-hepten-2-one			
CH ₃ C(O)CH ₃	0.706 ± 0.054^{D}	0.302 ± 0.048^{D}		
CH ₃ C(O)CH ₂ CH ₂ CHO	0.59 ± 0.13^{b}	0.82 ± 0.21^{b}		
OH		0.75 ^c		
tran	s-Cinnamaldehyde			
C ₆ H₅CHO	0.90 ± 0.39^{b}			
^a In the presence of suffic OH radicals formed. ^b Indica deviations combined with e	ient cyclohexane to so ated errors are two lea estimated overall unc	cavenge ≥95% of the ast-squares standard ertainties in the GC-		

deviations combined with estimated overall uncertainties in the GC-FID response factors for 6-methyl-5-hepten-2-one and acetone of \pm 5% each and in the relative GC-FID response factors of 6-methyl-5-hepten-2-one and CH₃C(O)CH₂CH₂CHO and of *trans*-cinnamaldehyde and benzaldehyde of \pm 20%. ^c Derived from the measured cyclohexanone plus cyclohexanol yield, assuming a formation yield of cyclohexanone plus cyclohexanol from cyclohexane of 0.50 (*12*). Estimated overall uncertainty is a factor of ~1.5.

The OH radical reaction with 6-methyl-5-hepten-2-one proceeds mainly (~95%) by initial addition to form the β -hydroxyalkyl radicals CH₃C(O)CH₂CH₂CH(OH)Ċ(CH₃)₂ and CH₃C(O)CH₂CH₂ĊHC(OH)(CH₃)₂, which rapidly add O₂ to yield the β -hydroxyalkyl peroxy radicals CH₃C(O)CH₂-CH₂CH(OH)C(OO)(CH₃)₂ and CH₃C(O)CH₂CH₂CH(OO)C-(OH)(CH₃)₂ (2). These β -hydroxyalkyl peroxy radicals then react with NO to form the β -hydroxynitrate or the corresponding β -hydroxyalkoxy radical plus NO₂ (2). The β -hydroxyalkoxy radical plus NO₂ (2). The β -hydroxyalkoxy radical formed from the decompose, with the α -hydroxy radical formed from the decomposition reaction reacting rapidly with O₂ to form the carbonyl CH₃C(O)CH₂CH₂CHO plus HO₂ radical (2):



1

$$\begin{array}{c} & \leftarrow CH_3C(O)\dot{C}HCH_2CH(OH)C(OH)(CH_3)_2 & (3a) \\ & \leftarrow CH_3C(O)CH_2CH_2\dot{C}HOH + CH_3C(O)CH_3 & (3b) \\ & & \downarrow O_2 \\ & & \downarrow O_2 \\ & & CH_3C(O)CH_2CH_2CHO + HO_2 \end{array}$$

The β -hydroxyalkoxy radical CH₃C(O)CH₂CH₂CH(O)C(OH)-(CH₃)₂ can react with O₂ or decompose (*2*):

CH₃C(O)CH₂CH₂CH(O)C(OH)(CH₃)₂



Our measured formation yields of acetone and CH₃C(O)CH₂CH₂CHO of 0.706 \pm 0.054 and 0.59 \pm 0.13, respectively, indicate that decomposition of the intermediate β -hydroxyalkoxy radicals dominates to form acetone plus CH₃C(O)CH₂CH₂CHO (reactions 3b and 4b). Other reaction processes, either hydroxynitrate formation from

the peroxy radical plus NO₂ reaction, isomerization of the $CH_3C(O)CH_2CH_2CH(OH)C(\dot{O})(CH_3)_2$ radical (reaction 3a), and/or reaction of the $CH_3C(O)CH_2CH_2CH(\dot{O})C(OH)(CH_3)_2$ radical with O₂ (reaction (4a) must also occur.

The O₃ reaction with 6-methyl-5-hepten-2-one proceeds by initial addition to form a primary ozonide (*2*), which then rapidly decomposes to either CH₃C(O)CH₃ plus the [CH₃C(O)CH₂CH₂ĊHOO]* biradical or to CH₃C(O)CH₂CH₂-CHO plus the [(CH₃)₂ĊOO]* biradical. Our measured acetone and CH₃C(O)CH₂CH₂CHO formation yields of 0.302 \pm 0.048 and 0.82 \pm 0.21, respectively, show that decomposition of the ozonide to CH₃C(O)CH₂CH₂CHO plus the [(CH₃)₂ĊOO]* biradical dominates and that the two pathways sum to unity within the experimental uncertainties. Our measured yield of OH radicals of ~0.75 is consistent with the formation of the [(CH₃)₂ĊOO]* biradical in ~70– 80% yield, followed by isomerization to the hydroperoxide [CH₃C(OOH)=CH₂]* and subsequent decomposition to form the OH radical in high yield (*12*, *20*):

$$[(CH_3)_2\dot{C}O\dot{O}]^* \rightarrow [CH_3C(OOH)=CH_2]^* \rightarrow CH_3C(O)\dot{C}H_2 + OH (5)$$

together with some additional formation of OH radicals from the $[CH_3C(O)CH_2CH_2\dot{C}HO\dot{O}]^*$ biradical. This is consistent with the O₃ reaction with 2,3-dimethyl-2-butene (*12, 20*), where the $[(CH_3)_2\dot{C}O\dot{O}]^*$ biradical leads to the formation of OH radicals in ~70–100% yield (*12, 20*).

trans-Cinnamaldehyde. GC-FID, GC-MS, and GC-FTIR analyses of irradiated CH₃ONO-NO-trans-cinnamaldehyde-air mixtures showed the formation of benzaldehyde, together with small amounts of cis-cinnamaldehyde formed from the photolysis of the trans-cinnamaldehyde. Our measured photolysis rate constant for trans-cinnamaldehyde was used to correct for the amounts of transcinnamaldehyde consumed by photolysis ($\sim 10-20\%$). Corrections for secondary reactions of benzaldehyde with the OH radical (19) used a rate constant for the OH radical reaction with benzaldehyde of $1.29 \times 10^{-11} \, cm^3 \, molecule^{-1}$ s^{-1} (2), with the corrections being $\leq 14\%$. Least-squares analyses of the amounts of benzaldehyde formed, corrected for reaction with the OH radical, against the amounts of trans-cinnamaldehyde reacted with the OH radical lead to the benzaldehyde formation yield given in Table 2. The amounts of cis-cinnamaldehyde formed were consistent with the amounts of trans-cinnamaldehyde photolyzed and our measured cis-cinnamaldehyde formation yield.

The OH radical reaction with *trans*-cinnamaldehyde is expected to proceed mainly by H-atom abstraction from the CHO group and initial addition to the >C=C< bond of the substituent group (2, 17).

OH + C₆H₅CH = CHCHO

$$H_2O + C_6H_5CH = CH\dot{C}O$$
(6a)
$$C_6H_5CH(OH)\dot{C}HCHO \text{ and } C_6H_5\dot{C}HCH(OH)CHO$$
(6b)

The β -hydroxyalkyl radicals C₆H₅CH(OH)ĊHCHO and

C₆H₅ĊHCH(OH)CHO are expected to react as discussed above for the β -hydroxyalkyl radicals formed from the OH radical reaction with 6-methyl-5-hepten-2-one, leading to the formation of benzaldehyde plus formaldehyde by decomposition of the intermediate β -hydroxyalkoxy radicals. The acyl radical C₆H₅CH=CHĊO formed in reaction 6a is expected to rapidly add O₂ to form the C₆H₅CH=CHC-(O)OO radical (2), which in the presence of NO is expected to also ultimately form, at least in part, benzaldehyde (2). Our measured high yield of benzaldehyde from the OH radical reaction with *trans*-cinnamaldehyde in the presence of NO is consistent with the above discussion, although we cannot assess the relative contributions of H-atom abstraction from the CHO group versus OH radical addition to the >C=C< bond of the substituent group.

Acknowledgments

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