

# Atmospheric Chemistry of Camphor

ANNI REISSELL, JANET AREY,\* AND ROGER ATKINSON\*.\*\*

Air Pollution Research Center, University of California, Riverside, California 92521

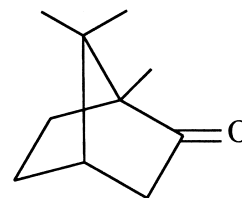
Received 28 January 2000; accepted 25 July 2000

**ABSTRACT:** Rate constants have been measured at  $296 \pm 2$  K for the gas-phase reactions of camphor with OH radicals,  $\text{NO}_3$  radicals, and  $\text{O}_3$ . Using relative rate methods, the rate constants for the OH radical and  $\text{NO}_3$  radical reactions were  $(4.6 \pm 1.2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $<3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively, where the indicated error in the OH radical reaction rate constant includes the estimated overall uncertainty in the rate constant for the reference compound. An upper limit to the rate constant for the  $\text{O}_3$  reaction of  $<7 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was also determined. The dominant tropospheric loss process for camphor is calculated to be by reaction with the OH radical. Acetone was identified and quantified as a product of the OH radical reaction by gas chromatography, with a formation yield of  $0.29 \pm 0.04$ . *In situ* atmospheric pressure ionization tandem mass spectrometry (API-MS) analyses indicated the formation of additional products of molecular weight 166 (dicarbonyl), 182 (hydroxydicarbonyl), 186, 187, 213 (carbonyl-nitrate), 229 (hydroxycarbonyl-nitrate), and 243. A reaction mechanism leading to the formation of acetone is presented, as are pathways for the formation of several of the additional products observed by API-MS.  
© 2000 John Wiley and Sons, Inc. *Int J Chem Kinet* 33: 56–63, 2001

## INTRODUCTION

Large quantities of nonmethane organic compounds (NMOC) are emitted into the atmosphere from vegetation, and on regional and global scales these vegetative emissions are estimated to dominate over NMOC emissions from anthropogenic sources [1–3]. Of these vegetative NMOC emissions, worldwide ~11% are attributed to monoterpenes [1], and for North America ~20% are attributed to monoterpenes plus sesquiterpenes [3]. The emissions of these vegetative NMOC have been shown to play an important role in the chemistry occurring on urban [4,5], regional [5–8], and global [9] scales. In the troposphere, NMOC present in the gas phase can undergo photolysis and reactions with OH radicals,  $\text{NO}_3$  radicals, and  $\text{O}_3$  [10], with the daytime OH radical reaction being an important, and often dominant, atmospheric loss process [10].

Although the atmospheric chemistry of many of the  $\text{C}_{10}\text{H}_{16}$  monoterpene hydrocarbons observed as vegetative emissions has been investigated [11,12], no data are available concerning the atmospheric chemistry of camphor, an oxygenated  $\text{C}_{10}$  monoterpene derivative that is the major compound emitted from Black Sage (*Salvia mellifera*) [13–15] and is also emitted from California Sagebrush (*Artemisia californica*) [15], European fir [16], and grassland [17]. Camphor has been reported to be present in ambient air at a number of locations throughout the world [18–20]. Accordingly, in this work, we have measured rate constants for the gas-phase reactions of camphor with OH radicals,  $\text{NO}_3$  radicals, and  $\text{O}_3$  at  $296 \pm 2$  K and have also investigated the products formed from the OH radical reaction in the presence of NO.



Camphor

Correspondence to: R. Atkinson (ratkins@mail.ucr.edu)

\* Also Interdepartmental Program in Environmental Toxicology and Department of Environmental Sciences

\*\* Also Department of Chemistry

© 2000 John Wiley & Sons, Inc.

## EXPERIMENTAL

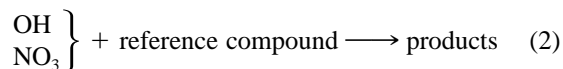
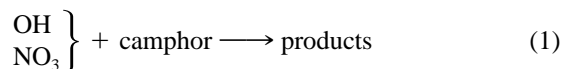
### Kinetic Studies

Experiments were carried out in a 7600-liter Teflon chamber, equipped with two parallel banks of black-lamps for irradiation, at  $296 \pm 2$  K and 740 Torr total pressure of purified air at  $\sim 5\%$  relative humidity. This chamber is fitted with a Teflon-coated fan to ensure rapid mixing of reactants during their introduction into the chamber. In all experiments, camphor was introduced into the chamber by flowing a stream of  $N_2$  gas through a Pyrex tube containing solid camphor.

Rate constants for the OH radical and  $NO_3$  radical reactions were determined using relative rate methods in which the relative disappearance rates of camphor and a reference compound, whose OH radical or  $NO_3$  radical reaction rate constant is reliably known, were measured in the presence of OH radicals or  $NO_3$  radicals [21]. Providing that camphor and the reference compound reacted only with OH radicals or  $NO_3$  radicals, then [21]

$$\ln\left(\frac{[\text{camphor}]_0}{[\text{camphor}]_t}\right) - D_t = \frac{k_1}{k_2} \left[ \ln\left(\frac{[\text{reference compound}]_0}{[\text{reference compound}]_t}\right) - D_t \right] \quad (I)$$

where  $[\text{camphor}]_0$  and  $[\text{reference compound}]_0$  are the initial concentrations of camphor and the reference compound, respectively, at time  $t = 0$ ,  $[\text{camphor}]_t$  and  $[\text{reference compound}]_t$  are the corresponding concentrations at time,  $t$ ,  $D_t$  is a factor to account for any dilution due to additions to the chamber during the reactions, and  $k_1$  and  $k_2$  are the rate constants for reactions (1) and (2), respectively.



OH radicals were generated by the photolysis of methyl nitrite ( $CH_3ONO$ ) in air at wavelengths  $>300$  nm [22], and NO was added to the reactant mixtures to suppress the formation of  $O_3$  and hence of  $NO_3$  radicals [22]. The initial reactant concentrations (in molecule  $cm^{-3}$  units) were:  $CH_3ONO$ ,  $(2.3-2.4) \times 10^{14}$ ; NO,  $(1.9-2.1) \times 10^{14}$ ; camphor  $(0.4-1.3) \times 10^{13}$ ; and *n*-octane (the reference compound),  $\sim 2.4 \times 10^{13}$ . Irradiations were carried out at 20% of the

maximum light intensity for 8–20 min. No additions were made to the chamber during the OH radical reactions, and therefore  $D_t = 0$  for these experiments.

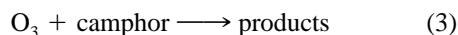
For measurement of the  $NO_3$  radical reaction rate constant,  $NO_3$  radicals were generated in the dark by thermal decomposition of  $N_2O_5$  in the presence of  $NO_2$  [23,24], and methacrolein was used as the reference compound. The initial reactant concentrations (in molecule  $cm^{-3}$  units) were: camphor,  $9 \times 10^{12}$ ; methacrolein,  $\sim 2.4 \times 10^{13}$ ;  $NO_2$ ,  $9.6 \times 10^{13}$ ; and two additions of  $N_2O_5$  (each addition corresponding to an initial  $N_2O_5$  concentration in the chamber of  $7.2 \times 10^{13}$  molecule  $cm^{-3}$ ) were made to the chamber during the experiment. The factor  $D_t$  to take into account dilution was  $D_t = 0.0028$  per  $N_2O_5$  addition to the chamber.

The concentrations of camphor and the reference compounds were measured during the experiments by gas chromatography with flame ionization detection (GC-FID). For the analysis of camphor, *n*-octane, and methacrolein, 100- $cm^3$  volume gas samples were collected from the chamber onto Tenax-TA solid adsorbent, with subsequent thermal desorption at  $\sim 225^\circ C$  onto a 30-m DB-1701 megabore column held at  $-40^\circ C$  and then temperature programmed to  $240^\circ C$  at  $8^\circ C \text{ min}^{-1}$ . Based on replicate analyses in the dark, the GC-FID measurement uncertainties for camphor were typically  $<2\%$ . GC-FID response factors for camphor, acetone (a reaction product; see below), and the reference compounds *n*-octane and methacrolein were determined by introducing measured amounts of the chemicals into the 7600-liter chamber and conducting several replicate GC-FID analyses [25]. NO and initial  $NO_2$  concentrations were measured using a Thermo Electron Corporation Series 14 chemiluminescent NO- $NO_x$  analyzer.

A rate constant, or upper limit thereof, for the reaction of camphor with  $O_3$  was determined in the dark by measuring the decay rate of camphor in the presence of a known concentration of  $O_3$  [26]. Cyclohexane was added to the reactant mixture to scavenge any OH radicals formed in the reaction system. Providing that any measured loss of camphor was due only to reaction with  $O_3$ , then

$$\ln([\text{camphor}]_0/[\text{camphor}]_t) = k_3[O_3](t - t_0) \quad (II)$$

where  $k_3$  is the rate constant for the reaction



The initial concentrations of camphor, cyclohexane, and  $O_3$  were  $1.2 \times 10^{13}$  molecule  $cm^{-3}$ ,  $7.2 \times 10^{14}$

molecule  $\text{cm}^{-3}$ , and  $5.7 \times 10^{13}$  molecule  $\text{cm}^{-3}$ , respectively, and the reaction was monitored for up to 3.8 h. The concentrations of camphor were measured by GC-FID as described above. Ozone concentrations were measured by ultraviolet absorption using a Dasibi 1003-AH ozone analyzer.

## Product Studies

A series of  $\text{CH}_3\text{ONO}$ – $\text{NO}$ –camphor–air irradiations were carried out as described above to investigate the products of the OH radical reaction using GC-FID and combined gas chromatography-mass spectrometry (GC-MS) for analyses. The initial reactant concentrations (in molecule  $\text{cm}^{-3}$  units) were:  $\text{CH}_3\text{ONO}$ ,  $(2.3-2.4) \times 10^{14}$ ;  $\text{NO}$ ,  $(1.4-2.4) \times 10^{14}$ ; and camphor,  $(0.9-1.8) \times 10^{13}$ . Irradiations were carried out at 20% of the maximum light intensity for 15–45 min, resulting in up to 25% reaction of the initially present camphor. The concentrations of camphor and reaction products were measured by GC-FID as described above. Gas samples were also collected onto Tenax-TA solid adsorbent for GC-MS analyses, with thermal desorption onto a 60-m DB-5 fused silica capillary column in a Hewlett Packard (HP) 5890 GC interfaced to a HP 5970 Mass Selective Detector and operated in the scanning mode.

$\text{CH}_3\text{ONO}$ – $\text{NO}$ –camphor–air irradiations were also carried out in a 7500-L Teflon chamber interfaced to a PE SCIEX API III MS/MS direct air sampling, atmospheric pressure ionization tandem mass spectrometer (API-MS). The chamber contents were sampled through a 25-mm diameter  $\times$  75-cm length Pyrex tube at  $\sim 20 \text{ L min}^{-1}$  directly into the API mass spectrometer source. The operation of the API-MS in the MS (scanning) and MS/MS [with collision-activated dissociation (CAD)] modes has been described previously [27,28]. Use of the MS/MS mode with CAD allows the “daughter ion” or “parent ion” spectrum of a given ion peak observed in the MS scanning mode to be obtained [27,28]. The positive ion mode was used in these API-MS and API-MS/MS analyses, with protonated water hydrates ( $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ ) generated by the corona discharge in the chamber diluent gas being responsible for the protonation of analytes. Ions are drawn by an electric potential from the ion source through the sampling orifice into the mass-analyzing first quadrupole or third quadrupole. In these experiments, the API-MS instrument was operated under conditions that favored the formation of dimer ions in the ion source region [27,28]. Neutral molecules and particles are prevented from entering the orifice by a flow of high-purity nitrogen (“curtain gas”), and as a

result of the declustering action of the curtain gas on the hydrated ions, the ions that are mass analyzed are mainly protonated molecular ions ( $[\text{M} + \text{H}]^+$ ) and their protonated homodimers and heterodimers [27,28]. The initial reactant concentrations (in molecule  $\text{cm}^{-3}$  units) were:  $\text{CH}_3\text{ONO}$ ,  $(0.3-2.5) \times 10^{13}$ ;  $\text{NO}$ ,  $(0.4-2.2) \times 10^{13}$ ; and camphor,  $\sim(0.2-2.4) \times 10^{13}$ . Irradiations were carried out for 8.5–10 min at 20% of the maximum light intensity.

## Chemicals

The chemicals used, and their stated purities, were: acetone (HPLC grade), Fisher Scientific; camphor (98%), methacrolein (95%) and *n*-octane (99+%), Aldrich Chemical Company; cyclohexane (high-purity solvent grade), American Burdick and Jackson; and  $\text{NO}$  ( $\geq 99.0\%$ ), Matheson Gas Products. Methyl nitrite and  $\text{N}_2\text{O}_5$  were prepared and stored as described previously [22,23], and  $\text{NO}_2$  was prepared just prior to use by reacting  $\text{NO}$  with an excess of  $\text{O}_2$ .  $\text{O}_3$  in  $\text{O}_2$  diluent was prepared as needed using a Welsbach T-408 ozone generator.

## RESULTS

### OH Radical Reaction Rate Constant

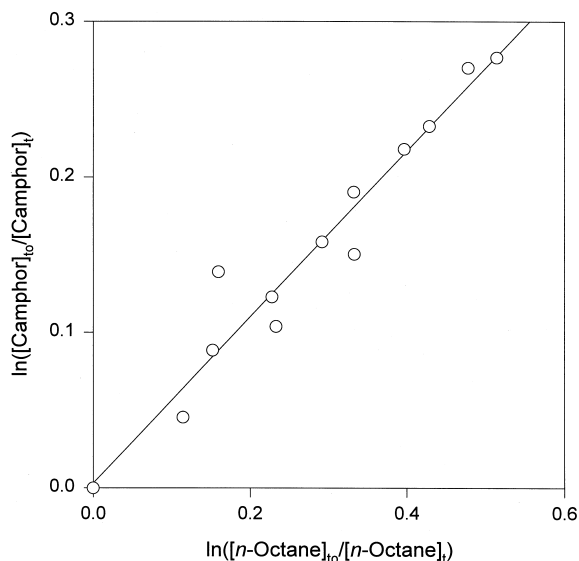
The camphor and *n*-octane concentrations measured by GC-FID during the  $\text{CH}_3\text{ONO}$ – $\text{NO}$ –camphor–*n*-octane–air irradiations are plotted in accordance with Eq. (I) in Figure 1. A reasonable straight-line plot is observed, and a least-squares analysis yields a rate constant ratio at  $296 \pm 2 \text{ K}$  of

$$\begin{aligned} k_1(\text{OH} + \text{camphor})/k_2(\text{OH} + n\text{-octane}) \\ = 0.534 \pm 0.079, \end{aligned}$$

where the indicated error is two least-squares standard deviations. This rate constant ratio is placed on an absolute basis by use of a rate constant  $k_2$  for the reaction of the OH radical with *n*-octane at 296 K of  $8.67 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  ( $\pm 20\%$ ) [11], resulting in a rate constant  $k_1$  at  $296 \pm 2 \text{ K}$  of

$$\begin{aligned} k_1(\text{OH} + \text{camphor}) = (4.6 \pm 1.2) \\ \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \end{aligned}$$

where the indicated error is two least-squares standard



**Figure 1** Plot of Eq. (I) for the gas-phase reaction of the OH radical with camphor, with *n*-octane as the reference compound.

deviations combined with the estimated overall uncertainty in the rate constant  $k_2$ .

### NO<sub>3</sub> Radical Reaction Rate Constant

GC-FID analyses of camphor and methacrolein in a reacting NO<sub>3</sub>–N<sub>2</sub>O<sub>5</sub>–NO<sub>2</sub>–camphor–methacrolein–air mixture showed that while up to 60% consumption of methacrolein occurred, <5% of the camphor reacted. This leads to an upper limit to the rate constant ratio at 296 ± 2 K of

$$k_1(\text{NO}_3 + \text{camphor})/k_2(\text{NO}_3 + \text{methacrolein}) < 0.06.$$

Using a rate constant  $k_2$  for the reaction of the NO<sub>3</sub> radical with methacrolein at 296 K of  $(3.3 \pm 1.0) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [29] leads to an upper limit for the rate constant  $k_1$  at 296 ± 2 K of

$$k_1(\text{NO}_3 + \text{camphor}) < 3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

### O<sub>3</sub> Reaction Rate Constant

The measured maximum loss of gas-phase camphor in the presence of  $5.7 \times 10^{13} \text{ molecule cm}^{-3}$  of O<sub>3</sub> over a period of 3.8 h was <2%, and within the analytical uncertainties. Assuming a maximum loss of camphor

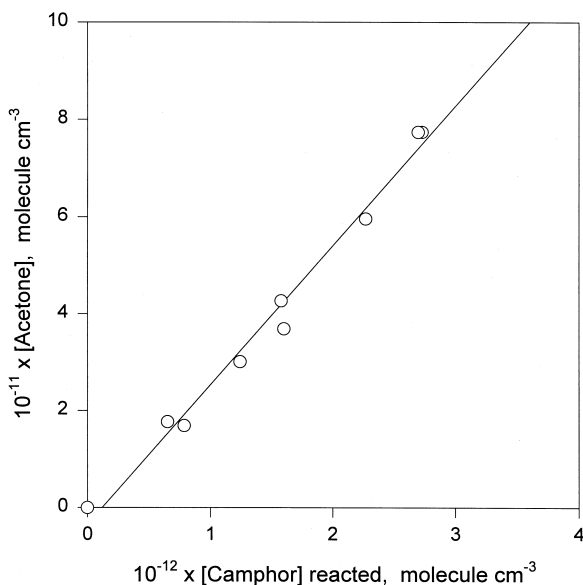
due to reaction with O<sub>3</sub> of 5% leads to an upper limit to the rate constant  $k_3$  at 296 ± 2 K of

$$k_3(\text{O}_3 + \text{camphor}) < 7 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

### Products of the OH Radical Reaction

GC-FID and GC-MS analyses of irradiated CH<sub>3</sub>ONO–NO–camphor–air mixtures showed the formation of acetone, which was identified by matching its GC retention time and mass spectrum with those of an authentic standard. While acetone also reacts with the OH radical [30], corrections for secondary reactions of acetone with the OH radical were <1% and were ignored. A plot of the amounts of acetone formed against the amounts of camphor reacted is shown in Figure 2, and a least-squares analysis leads to a molar formation yield of acetone from camphor of  $0.29 \pm 0.04$ , where the indicated error is two least-squares standard deviations combined with estimated overall uncertainties in the GC-FID response factors for camphor and acetone of ±5% each.

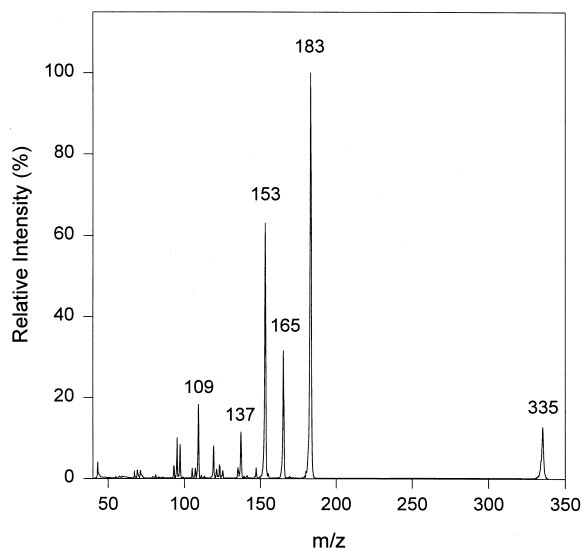
API-MS and API-MS/MS analyses of irradiated CH<sub>3</sub>ONO–NO–camphor–air mixtures were also carried out. API-MS/MS “daughter ion” and “parent ion” spectra were obtained for peaks observed in the API-MS analyses. Product ion peaks were identified based on the observation of homo- or hetero-dimer ions (e.g., [M<sub>C</sub> + M<sub>P</sub> + H]<sup>+</sup>, where M<sub>C</sub> and M<sub>P</sub> are camphor and a product, respectively) in the API-MS/MS “parent



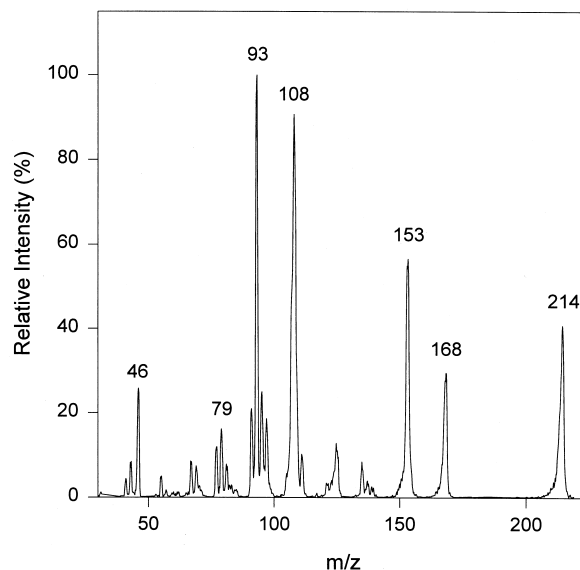
**Figure 2** Plot of the amounts of acetone formed against the amounts of camphor reacted with the OH radical.

ion" spectra and consistency of the API-MS/MS "daughter ion" spectrum of a homo- or hetero-dimer ion with the "parent ion" spectra of the constituent  $[M_C + H]^+$  and  $[M_P + H]^+$  ion peaks [27,28].

API-MS/MS "parent ion" spectra of the 153 u protonated camphor ion peak showed the presence of dimer ions at 211, 305, 319, 335, 339, 366, 382 and 396 u, with the 305 u ion peak being the protonated camphor dimer ion and the 211 u ion peak being attributed to  $[\text{camphor} + \text{acetone} + H]^+$ . The remaining dimer ion peaks are attributed to the presence of products of molecular weight 166, 182, 186, 213, 229 and 243. API-MS/MS "daughter ion" spectra of these dimer ion peaks were consistent with the formation of these suggested products, as shown for example in Figure 3 for the 335 u ion peak showing the presence of the protonated molecular weight 182 product at 183 u. The products of molecular weight 213, 229, and 243 must contain a nitrogen atom and are hence anticipated to be organic nitrates,  $\text{RONO}_2$ .  $[M + H]^+$  ion peaks of these products were also present at 214, 230, and 244 u, and API-MS/MS "daughter ion" spectra of these  $[M + H]^+$  peaks each showed fragment ions from a loss of  $\text{NO}_2$  and the presence of a fragment ion at 46 u ( $\text{NO}_2^+$ ), consistent with their assignment as organic nitrates (see, e.g., Figure 4 for an API-MS/MS "daughter ion" spectrum of the 214 u ion peak). In addition, the API-MS spectra indicated a product ion peak at 188 u whose API-MS/MS "daughter ion" spectrum



**Figure 3** API-MS/MS CAD "daughter ion" spectrum of the 335 u ion peak observed in the API-MS spectra of irradiated  $\text{CH}_3\text{ONO}-\text{NO}-\text{camphor}$ -air mixtures. The 335 u ion is attributed to a protonated dimer of (camphor + molecular weight 182 product), and the fragment ions at 153 and 183 are then  $[\text{camphor} + H]^+$  and  $[182 + H]^+$ , respectively.



**Figure 4** API-MS/MS CAD "daughter ion" spectrum of the 214 u ion peak observed in the API-MS spectra of irradiated  $\text{CH}_3\text{ONO}-\text{NO}-\text{camphor}$ -air mixtures. The fragment ion at 168 u corresponds to a loss of  $\text{NO}_2$ , and the fragment ion at 46 u is attributed to  $\text{NO}_2^+$  leading to the tentative identification of this molecular weight 213 product as an organic nitrate.

was consistent with an organic nitrate of molecular weight 187.

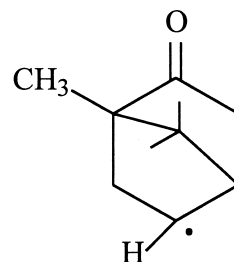
## DISCUSSION

Our measured upper limits to the rate constants for the reactions of camphor with  $\text{NO}_3$  radicals and  $\text{O}_3$  are consistent with literature data for other ketones not containing unsaturated  $\text{>C=C<}$  bonds [30–32], in that no reaction of  $\text{O}_3$  with such ketones has been observed [30–32] and the  $\text{NO}_3$  radical reactions are very slow [30,32]. Our measured rate constant for the OH radical reaction is a factor of 2.2 lower than the value of  $9.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  calculated using the estimation method of Kwok and Atkinson [33]. Our measured rate constants, or upper limits thereof, can be combined with ambient atmospheric concentrations of OH radicals,  $\text{NO}_3$  radicals, and  $\text{O}_3$  to provide lifetimes of camphor with respect to each of these chemical loss processes. Using tropospheric concentrations of: OH radicals, a 24-h average of  $1.0 \times 10^6 \text{ molecule cm}^{-3}$  [34,35];  $\text{NO}_3$  radicals, a 24-h average of  $2.5 \times 10^8 \text{ molecule cm}^{-3}$  [36]; and  $\text{O}_3$ , a 24-h average of  $7 \times 10^{11} \text{ molecule cm}^{-3}$  [37], the calculated lifetimes of camphor due to reaction with OH radicals,  $\text{NO}_3$  radicals, and  $\text{O}_3$  are 2.5 days, >150 days, and >230 days, respectively. Clearly, reaction with the

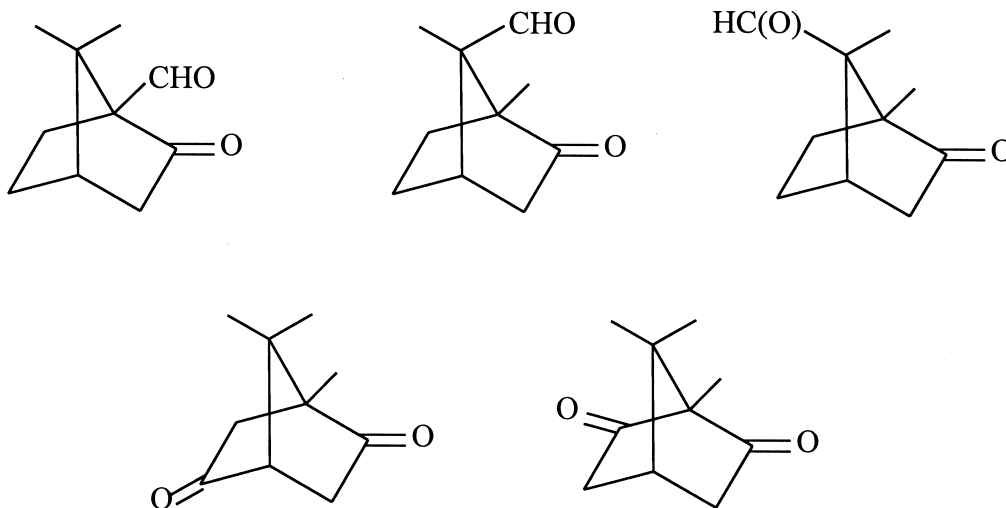
OH radical is the dominant chemical loss process for camphor in the troposphere.

In the presence of NO (such that organic peroxy radicals dominantly react with NO), the products of the OH radical-initiated reaction are acetone in  $29 \pm 4\%$  yield, together with products of molecular weight 166, 182, 186, 187, 213, 229, and 243. The products of molecular weight 166 and 182 have formulas of  $C_{10}H_{14}O_2$  and  $C_{10}H_{14}O_3$ , respectively (note that camphor is  $C_{10}H_{16}O$  and of molecular weight 152), and we suggest these are a dicarbonyl and a hydroxydicarbonyl, respectively. The molecular weight 213 and 229 products have formulas of  $C_{10}H_{15}O(ONO_2)$  and  $C_{10}H_{15}O_2(ONO_2)$ , respectively, and are attributed to a carbonyl-nitrate and a hydroxycarbonyl-nitrate, re-

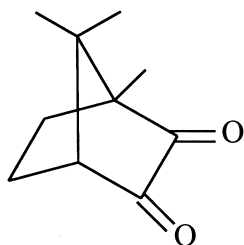
spectively. The formation of these products is illustrated in Scheme I for the structure  $RCH_2CCCH_2R'$ , where  $RCH_2CCC^*HR'$  could, for example, be



The molecular weight 166 dicarbonyl products are expected to include



but not



because alkoxy radicals of structure  $>C(O^*)C(=O)-$  decompose rapidly [11,30]. As shown in Scheme I, the formation of the molecular weight 182 and 229 products indicates the occurrence of an alkoxy radical isomerization reaction. The products of molecular

weight 186, 187, and 243 are consistent with formulas of  $C_9H_{14}O_4$ ,  $C_8H_{13}O(ONO_2)$ , and  $C_{10}H_{13}O_3(ONO_2)$ , respectively, but whether or not these are primary (first-generation) products or arise from subsequent reactions of first-generation products is not presently known.

The formation of acetone is anticipated to occur after initial H-atom abstraction from the tertiary C—H bond, as shown in Scheme II. H-atom abstraction from this tertiary C—H bond is predicted to be significant, being calculated to account for 47% of the overall reaction [33]. Given the factor of 2 discrepancy in the prediction of the overall OH radical reaction rate constant (see above), it is entirely possible that acetone [plus its co-product(s)] is the dominant product formed subsequent to this H-atom abstraction channel.



21. Aschmann, S. M.; Atkinson, R. *Int J Chem Kinet* 1998, 30, 533.
22. Atkinson, R.; Carter, W. P. L.; Winer, A. M.; Pitts, J. N., Jr., *J Air Pollut Control Assoc* 1981, 31, 1090.
23. Atkinson, R.; Plum, C. N.; Carter, W. P. L.; Winer, A. M.; Pitts, J. N., Jr. *J Phys Chem* 1984, 88, 1210.
24. Atkinson, R.; Aschmann, S. M.; Pitts, J. N., Jr. *J Phys Chem* 1988, 92, 3454.
25. Atkinson, R.; Tuazon, E. C.; Aschmann, S. M., *Environ Sci Technol* 1995, 29, 1674.
26. Atkinson, R.; Aschmann, S. M.; Winer, A. M.; Pitts, J. N., Jr. *Int J Chem Kinet* 1981, 13, 1133.
27. Aschmann, S. M.; Chew, A. A.; Arey, J.; Atkinson, R. *J Phys Chem A* 1997, 101, 8042.
28. Aschmann, S. M.; Reissell, A.; Atkinson, R.; Arey, J. *J Geophys Res* 1998, 103, 25553.
29. Chew, A. A.; Atkinson, R.; Aschmann, S. M. *J Chem Soc, Faraday Trans* 1998, 94, 1083.
30. Atkinson, R. *J Phys Chem Ref Data* 1994, Monograph 2, 1.
31. Atkinson, R.; Carter, W. P. L. *Chem Rev* 1984, 84, 437.
32. Alvarado, A.; Arey, J.; Atkinson, R. *J Atmos Chem* 1998, 31, 281.
33. Kwok, E. S. C.; Atkinson, R. *Atmos Environ* 1995, 29, 1685.
34. Prinn, R. G.; Weiss, R. F.; Miller, B. R.; Huang, J.; Alyea, F. N.; Cunnold, D. M.; Fraser, P. J.; Hartley, D. E.; Simmonds, P. G. *Science* 1995, 269, 187.
35. Hein, R.; Crutzen, P. J.; Heimann, M. *Global Biogeochem Cycles* 1997, 11, 43.
36. Atkinson, R. *J Phys Chem Ref Data* 1991, 20, 459.
37. Logan, J. A. *J Geophys Res* 1985, 90, 10463.