H-Atom Abstraction from Selected C–H Bonds in 2,3-Dimethylpentanal, 1,4-Cyclohexadiene, and 1,3,5-Cycloheptatriene

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ABSTRACT: The gas-phase reactions of OH radicals with 1,4-cyclohexadiene, 1,3,5cycloheptatriene, and 2,3-dimethylpentanal have been investigated to determine the importance of H-atom abstraction at specific positions in these molecules. Benzene was observed as a product of the reaction of OH radicals with 1,4-cyclohexadiene in 12.5 \pm 1.2% yield, in good agreement with a previous study and indicating that this is the fraction of the reaction proceeding by H-atom abstraction from the allylic C-H bonds. In contrast, no formation of tropone from 1,3,5-cycloheptatriene was observed, suggesting that in this case Hatom abstraction is not important. For the reaction of OH radicals with 2,3-dimethylpentanal, formation of 3-methyl-2-pentanone was observed in 5.4 \pm 1.0% yield (after correction for reaction of 3-methyl-2-pentanone with OH radicals), and this product is predicted to be formed after initial H-atom abstraction from the 2-position CH group. Acetaldehyde and 2-butanone were also observed as products, with initial yields of \sim 90% and \sim 26%, respectively, and their formation appeared to involve, at least in part, an intermediary acyl peroxy radical. Using a relative rate method, the measured rate constants for the reactions of OH radicals with 2,3-dimethylpentanal, 3-methyl-2-pentanone, and tropone are (in units of 10^{-12} cm³ molecule $^{-1}$ s $^{-1}$) 2,3-dimethylpentanal, 42 \pm 7; 3-methyl-2-pentanone, 6.87 \pm 0.08; and tropone, 42 ± 6 . © 2003 Wiley Periodicals, Inc. Int J Chem Kinet 35: 415–426, 2003

INTRODUCTION

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For many volatile organic compounds (VOCs) emitted into the atmosphere, daytime reaction with the OH radical is an important, and often dominant, transformation process [1]. For alkanes, alkenes, aromatic hydrocarbons, and oxygenated compounds, these OH radical reactions proceed by H-atom abstraction from

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C-H and O-H bonds, by OH radical addition to the carbon atoms of C=C bonds, and by OH radical addition to the carbon atoms of aromatic rings [1-6]. While the overall rate constants for the gas-phase reactions of OH radicals with over 500 VOCs have been measured [3], the partial rate constants for H-atom abstraction from the various C-H (or O-H) bonds are known only for a small subset of these VOCs. These partial rate data have been obtained from, for example, kinetic studies of alkanes [7-10], alcohols [11–13], methyl hydroperoxide [14], and toluene [15], using partially and fully deuterated VOCs or using ¹⁶OH and ¹⁸OH radicals, and from product studies of a number of VOCs (for example, 1,3- and 1,4cyclohexadiene [16], *n*-pentane [17], diethyl ether [2], methyl tert-butyl ether [2], and selected diols [18] and alcohols [19-22]).

The major focus of this study was to investigate the importance of H-atom abstraction from sites in an aliphatic aldehyde other than from the CHO group. For the reaction of OH radicals with acetaldehyde, the major reaction pathway involves H-atom abstraction from the CHO group [23],

$$OH + CH_3CHO \rightarrow H_2O + CH_3C^{\bullet}O$$
 (1)

and it is generally accepted that H-atom abstraction from the CHO group dominates for higher aldehydes such as propanal and butanal [3], although no data are presently available to confirm this. The potential mechanisms of a number of commercially available aldehydes were reviewed, using empirical predictive methods [24,25], to assess which aldehyde(s) could lead to a product or products which would be unique to H-atom abstraction from C-H bond(s) other than that on the CHO group. 2,3-Dimethylpentanal [CH₃CH₂CH(CH₃)CH(CH₃)CHO] appeared to fit this criteria, with H-atom abstraction from the 2-position CH group being predicted [24,25] to lead, in the presence of O₂ and NO, only to formation of 3-methyl-2-pentanone, a product which is predicted not to be formed to any significant extent after H-atom abstraction from any other C-H bond in 2,3-dimethylpentanal. Accordingly, in this work we have investigated the kinetics and products of the reaction of OH radicals with 2,3dimethylpentanal. In addition, we have investigated the importance of H-atom abstraction by OH radicals from the allylic C-H bonds in 1,4-cyclohexadiene and 1,3,5-cycloheptatriene by measuring the formation yields of benzene from 1,4-cyclohexadiene and of tropone (2,4,6-cycloheptatrienone) from 1,3,5cycloheptatriene, noting that Ohta [16] previously observed the formation of benzene from the OH radicalinitiated reaction of 1,4-cyclohexadiene in 15% yield (and from 1,3-cyclohexadiene in 7% yield).

EXPERIMENTAL METHODS

Experiments to measure the rate constant for the reaction of OH radicals with 2,3-dimethylpentanal and to investigate the formation of selected products from the OH radical-initiated reactions of 2,3-dimethylpentanal, 1,4-cyclohexadiene, and 1,3,5-cycloheptatriene were carried out at 298 \pm 2 K and 740 Torr total pressure of synthetic air (80% $N_2 + 20\% O_2$) in a 5870 L evacuable, Teflon-coated chamber equipped with an in situ multiple-reflection optical system interfaced to a Mattson Galaxy 5020 FT-IR spectrometer. Irradiation was provided by a 24-kW xenon arc lamp, with the light being filtered through a 6-mm thick Pyrex pane to remove wavelengths <300 nm. The chamber was fitted with two Teflon-coated fans to ensure rapid mixing of reactants during their introduction into the chamber. IR spectra were recorded with 32 scans per spectrum (corresponding to 1.2 min averaging time), a full-widthat-half-maximum resolution of 0.7 cm^{-1} , and a path length of 62.9 m.

Preliminary experiments on the OH radicalinitiated reactions of 2,3-dimethylpentanal and 1,3,5cycloheptatriene and experiments to measure the rate constants for the reactions of OH radicals with 3methyl-2-pentanone and tropone and to determine the formation yield of benzene from 1,4-cyclohexadiene were carried out at 298 ± 2 K and 740 Torr total pressure of purified air (at $\sim 5\%$ relative humidity) in a 7000 L Teflon-coated chamber equipped with two parallel banks of blacklamps for irradiation and a Tefloncoated fan to ensure rapid mixing of reactants during their introduction into the chamber. Analyses were made by gas chromatography with flame ionization detection (GC-FID). For the analysis of n-octane, methyl vinyl ketone, acetaldehyde, 2-butanone, 3-methyl-2pentanone, and tropone, 100-cm³ volume gas samples were collected from the chamber onto Tenax-TA solid adsorbent with subsequent thermal desorption at ~250°C onto a 30 m DB-1701 megabore column held at -40° C and then temperature programmed to 200°C at 8°C min⁻¹ (this is denoted the solid adsorbent/thermal desorption procedure). For the analysis of 1,4-cyclohexadiene and benzene, gas samples were collected from the chamber into a 100-cm³ volume all-glass, gas-tight syringe with subsequent transfer via a 1-cm³ gas sampling valve onto a 30-m DB-5 megabore column held at -25°C and then temperature programmed to 200°C at 8°C min⁻¹ (this is denoted the gas transfer/gas sampling valve procedure).

Kinetic Studies

Rate constants for the reactions of OH radicals with 2,3-dimethylpentanal, 3-methyl-2-pentanone, and tropone were determined using a relative rate technique, in which the relative decays of the carbonyl compound and a reference compound, whose OH radical reaction rate constant is reliably known, were measured in the presence of OH radicals. Provided that the carbonyls and the reference compound reacted only with OH radicals, then,

$$\ln\left(\frac{[\text{carbonyl}]_{t_0}}{[\text{carbonyl}]_t}\right) = \frac{k_2}{k_3} \ln\left(\frac{[\text{reference compound}]_{t_0}}{[\text{reference compound}]_t}\right)$$
(I)

where [carbonyl]_{t_0} and [reference compound]_{t_0} are the concentrations of 2,3-dimethylpentanal, 3-methyl-2pentanone, or tropone and reference compound at time t_0 , respectively; [carbonyl]_t and [reference compound]_t are the corresponding concentrations at time t; and k_2 and k_3 are the rate constants for reactions (2) and (3), respectively.

$$OH + carbonyl \rightarrow products$$
 (2)

$$OH + reference compound \rightarrow products$$
 (3)

Hydroxyl radicals were generated in the presence of NO by the photolysis of CH_3ONO in air at wavelengths >300 nm [25].

The initial reactant concentrations for the experiments involving 2,3-dimethylpentanal carried out in the evacuable chamber were (in molecule cm⁻³) as follows: CH₃ONO, 2.46 × 10¹⁴; NO, 2.46 × 10^{14} ; 2,3-dimethylpentanal, (2.36–2.41) × 10^{14} ; and 2-methylpropene (the reference compound), (1.84–2.46) × 10^{14} . Irradiations were carried out intermittently in 6-min periods, with IR spectra being recorded during the dark periods and with total irradiation times of 18 min.

For experiments carried out in the Teflon chamber, the initial reactant concentrations (in molecule cm⁻³) were as follows: CH₃ONO, $\sim 2.4 \times 10^{14}$; NO, $\sim 2.4 \times 10^{14}$; 3-methyl-2-pentanone or tropone, $\sim 2.4 \times 10^{13}$; and *n*-octane or methyl vinyl ketone (the reference compounds), $\sim 2.4 \times 10^{13}$. Irradiations were carried out for 3–45 min, resulting in the reaction of up to 39–73% of the carbonyls or reference compounds. The concentrations of 3-methyl-2-pentanone, tropone, *n*-octane, and methyl vinyl ketone were measured by GC–FID, using the solid adsorbent/thermal desorption procedure.

Product Studies

Experiments in the Teflon chamber with GC analyses were conducted as described earlier for the kinetic experiments, with similar initial reactant concentrations and GC–FID analysis procedures, except that no reference compound was present.

For the experiments conducted in the evacuable chamber with in situ FT-IR analyses, the initial reactant concentrations (in molecule cm^{-3}) were as follows: CH₃ONO, 2.46 \times 10¹⁴; NO, 2.46 \times 10^{14} ; 2,3-dimethylpentanal, (2.35–2.41) × 10^{14} ; 1,4cvclohexadiene, 3.69×10^{14} (including the benzene impurity initially present); or 1,3,5-cycloheptatriene, 2.46×10^{14} . 2-Methylpropene was present in two of the three 2,3-dimethylpentanal experiments at an initial concentration of $(1.84-2.46) \times 10^{14}$ molecule cm^{-3} . For 2,3-dimethylpentanal, the three experiments involved intermittent irradiation (6-10-min duration each) with IR spectra being recorded during the dark periods and with total irradiation times of 18-28 min. For 1,3,5-cycloheptatriene, one experiment was carried out with intermittent irradiation (1-5-min duration) for a total irradiation time of 20 min. For 1,4cyclohexadiene, one irradiation was carried out with continuous irradiation for 15 min.

Because of the difficulties in quantifying the carbonyl products from the 2,3-dimethylpentanal reaction solely by FT-IR spectroscopy, concurrent GC–FID analyses, using the solid adsorbent/thermal desorption procedure, were carried out. These GC–FID analyses for specific carbonyl products were used as a basis for subtracting the spectral contributions of these compounds from the total product spectra (see later), thus facilitating the FT-IR analyses of other species, including the parent compound.

Chemicals

The sources and stated purities of the chemicals used were 2,3-dimethylpentanal (93%) from Chemsampco; 1,4-cyclohexadiene (97%), 1,3,5-cycloheptatriene (90%), tropone (97%), 2-butanone (99%), 3-methyl-2-pentanone (99%), and acetaldehyde (99.5+%) from Aldrich; benzene (99.9+%) from American Burdick and Jackson; and NO (\geq 99.0%) from Matheson Gas Products. All of these compounds were used as received, except for 2,3-dimethylpentanal, which was fractionated in a vacuum line with a middle fraction being collected and used for the experiments. Methyl nitrite was prepared as described by Taylor et al. [26] and stored under vacuum at 77 K.

RESULTS

1,4-Cyclohexadiene

Preliminary experiments in the Teflon chamber with analyses by GC-FID, using the solid adsorbent/thermal desorption procedure, showed significant artifact formation of benzene from 1,4-cyclohexadiene during the sampling and analysis procedure, presumably from decomposition of 1,4-cyclohexadiene during the thermal desorption procedure. However, GC-FID analyses involving transfer of gas samples onto the GC column via a gas sampling valve showed no evidence for such artifact benzene formation (although benzene was observed to be present in the 1,4-cyclohexadiene sample used, at levels of 2.6% and 6.3% in the two independent sets of experiments conducted using GC-FID analyses). Two sets of experiments were carried out, with independent calibrations of the GC-FID response factors for 1,4-cyclohexadiene and benzene, and plots of the amounts of benzene formed (i.e., taking into account the benzene initially present in the 1,4-cyclohexadiene samples) against the amounts of 1,4-cyclohexadiene reacted are shown in Fig. 1. Corrections for secondary reaction of benzene with OH radicals were negligible (<1%). The benzene formation yields obtained from least-squares analyses of the data from these two sets of experiments were $12.7 \pm 2.4\%$ and $12.6 \pm 1.5\%$, where the indicated errors are two least-squares standard deviations combined with estimated overall uncertainties in the GC-FID response factors for 1,4-cyclohexadiene and benzene of $\pm 5\%$ each.

A vapor sample of 1,4-cyclohexadiene introduced into the evacuable chamber initially contained 7.1% benzene, as analyzed by in situ FT-IR spectroscopy. The sharp Q-branch of benzene at 674 cm⁻¹ and the series of sharp peaks of 1,4-cyclohexadiene at around ~960 cm⁻¹ were used for IR analyses. Irradiation of a CH₃ONO–NO–1,4-cyclohexadiene–air mixture resulted in a benzene yield of 12.2 \pm 2.2% (see the plot in Fig. 1), where the indicated error is two least-squares standard deviations combined with \pm 4% and \pm 7% estimated uncertainties in the IR analyses of 1,4-cyclohexadiene and benzene, respectively.

1,3,5-Cycloheptatriene

Preliminary experiments in the Teflon chamber with analyses by GC-FID using the solid adsorbent/thermal



Figure 1 Plots of the amounts of benzene formed (taking into account the benzene initially present in the 1,4-cyclohexadiene samples) against the amounts of 1,4-cyclohexadiene reacted with the OH radical. (\Box , \odot) Analyses by GC–FID (two independent sets of experiments with three experiments per set); (\triangle) analyses by in situ FT-IR spectroscopy from a single experiment. Data with \Box and Δ symbols have been displaced vertically by 1.0 and 0.5 units, respectively, for clarity.

desorption procedure showed significant artifact formation of tropone from cycloheptatriene during the sampling and analysis procedure, presumably from oxidation of cycloheptatriene during the thermal desorption procedure. Furthermore, tropone could not be analyzed by GC–FID involving transfer of gas samples onto the GC column via a gas sampling valve (no GC peak was observed, presumably due to adsorption of tropone to the surfaces of the gas sampling valve and/or syringe). It was hence not possible to investigate the formation of tropone from the OH radical-initiated reaction of cycloheptatriene using GC for analysis, and experiments were therefore carried out in the evacuable chamber with analyses by in situ FT-IR spectroscopy.

However, tropone could be reliably analyzed in the absence of cycloheptatriene by GC–FID, using the solid adsorbent/thermal desorption procedure. Accordingly, the rate constant for the reaction of OH radicals with tropone was measured using the relative rate method, with methyl vinyl ketone as the reference compound. The data obtained from three experiments are plotted in accordance with Eq. (I) in Fig. 2, and a least-squares analysis yields the rate constant ratio k_2/k_3 and rate constant k_2 given in Table I.



Figure 2 Plot of Eq. (I) for the reaction of OH radicals with tropone, with methyl vinyl ketone as the reference compound. Analyses were by GC–FID.

In the experiment with in situ FT-IR spectroscopic analyses, after subtraction of IR absorption bands of the remaining cycloheptatriene (52% of the initial amount) and CH₃ONO and of the photooxidation products NO₂, HCHO, HC(O)OH, HNO₃, and CH₃ONO₂, no evidence for the formation of tropone or of its isomer benzaldehyde was obtained. The IR analyses of cycloheptatriene, tropone, and benzaldehyde were based on their distinct peaks at 709, 1656, and 688 cm^{-1} , respectively. After taking into account secondary reactions of tropone and benzaldehyde with OH radicals, using rate constants for the reactions of OH radicals with cycloheptatriene, tropone and benzaldehyde (in units of 10^{-11} cm³ molecule⁻¹ s⁻¹) of 9.95 [4], 4.2 (Table I) and 1.6 [2], respectively, upper limits to the formation yields of tropone and benzaldehyde from cycloheptatriene of <1.2% and <0.7%, respectively, were obtained.

2,3-Dimethylpentanal

Initial GC-FID analyses of 2,3-dimethylpentanal, using the solid adsorbent/thermal desorption procedure, showed no analytical problems in the absence of NO_x , with no decrease in the 2,3-dimethylpentanal concentration in the dark over a period of several hours. However, in the presence of NO_x , the 2,3-dimethylpentanal GC peak area was observed to decrease with time, gradually leveling off after \sim 4 h to a value 40–45% lower than the initial analysis, with a concurrent increase in the GC-FID peak area of 2-butanone (but not of 3methyl-2-pentanone) over this time period. Because analogous experiments with in situ FT-IR analysis did not show this behavior, it appears that degradation of 2,3-dimethylpentanal occurs in the presence of NO_x , presumably due to reaction with NO2 on the Tenax solid adsorbent during sampling and/or thermal desorption.

Therefore experiments to measure the rate constant for the reaction of OH radicals with 2,3dimethylpentanal and to investigate the products formed were carried out in the evacuable chamber with in situ FT-IR analyses of 2,3-dimethylpentanal (and certain other species). In these experiments the infrared analyses involved subtraction of absorption bands by the unreacted CH₃ONO and its photolysis products in the presence of NO (i.e., HCHO, CH₃ONO₂, HNO₃, HONO, HCOOH, H₂O, and NO₂). The analysis of 2,3dimethylpentanal utilized its strongest band at 1743 cm⁻¹ but required prior subtraction of overlapped absorption bands by 2-butanone, 3-methyl-2-pentanone, and acetaldehyde, as well as by acetone when 2methylpropene was a component of the irradiated mixture. Subtraction of the CH₃CHO absorption bands was based on its sharp absorption feature at 1352 cm^{-1} . Subtractions of the absorption bands by 2-butanone and 3-methyl-2-pentanone using calibrated spectra were based on their concurrent analyses by GC-FID. 2-Methylpropene, used as the reference compound in the kinetic experiments, was analyzed by its weak, but sharp, peak at 890 cm^{-1} , while the absorption bands of

Table I Rate Constant Ratios k_2/k_3 and Rate Constants k_2 (cm³ molecule⁻¹ s⁻¹) for the Gas-Phase Reactions of OH Radicals with Tropone, 2,3-Dimethylpentanal, and 3-Methyl-2-pentanone at 298 ± 2 K

Carbonyl	Reference Compound	k_2/k_3^a	$10^{12} \times k_2{}^{a,b}$
Tropone 2,3-Dimethylpentanal 3 Methyl 2 pentanone	Methyl vinyl ketone 2-Methylpropene	2.07 ± 0.29 0.82 ± 0.13 0.789 ± 0.009	42 ± 6 42 ± 7 6.87 ± 0.08

^{*a*} Indicated uncertainties are two least-squares standard deviations, except for 2,3-dimethylpentanal where an additional $\pm 15\%$ uncertainty in k_2/k_3 (0.815 \pm 0.032 with two least-squares uncertainties) has been included to account for possible additional errors in the subtraction procedure.

^b Placed on an absolute basis by use of rate constants k_3 (cm³ molecule⁻¹ s⁻¹) at 298 K of k_3 (methyl vinyl ketone = 2.01×10^{-11} [27], k_3 (2-methylpropene) = 5.14×10^{-11} [4], and k_3 (*n*-octane) = 8.71×10^{-12} [4]. The cited rate constants k_2 do not include the uncertainties (estimated to be $\sim \pm 10\%$) in the rate constants k_3 .

its main oxidation product $CH_3C(O)CH_3$ (along with HCHO) were subtracted based on its distinct band at 1365 cm⁻¹.

Rate constants for the reactions of OH radicals with 2,3-dimethylpentanal and 3-methyl-2-pentanone were measured using the relative rate method, with 2-methylpropene and *n*-octane as the reference compounds, respectively. Data from CH₃ONO–NO–2,3-dimethylpentanal–2-methylpropene–air irradiations carried out in the evacuable chamber with in situ FT-IR analyses and from CH₃ONO–NO–3-methyl-2-pentanone–*n*-octane–air irradiations carried out in the Teflon chamber with GC–FID analyses are plotted in accordance with Eq. (I) in Fig. 3. The rate constant ratios k_2/k_3 and rate constants k_2 obtained from these data by least-squares analyses are given in Table I.

Products of the reaction of OH radicals with 2,3dimethylpentanal were also identified and quantified in the two CH₃ONO–NO–2,3-dimethylpentanal– 2-methylpropene–air irradiations and in an additional CH₃ONO–NO–2,3-dimethylpentanal–air irradiation. As noted earlier, the concentrations of 2,3dimethylpentanal during the experiments were measured by FT-IR spectroscopy and the concentrations of 2-butanone and 3-methyl-2-pentanone were measured



Figure 3 Plots of Eq. (I) for the reactions of OH radicals with 3-methyl-2-pentanone and 2,3-dimethylpentanal, with *n*-octane and 2-methylpropene as the reference compounds, respectively. Analyses of 3-methyl-2-pentanone and *n*-octane were by GC–FID, and of 2,3-dimethylpentanal and 2-methylpropene were by in situ FT-IR spectroscopy. Data for the 2,3-dimethylpentanal reaction are displaced vertically by 0.1 unit for clarity and the differing symbols for this reaction denote the individual experiments.

by GC–FID. The acetaldehyde concentrations were determined by both FT-IR and GC–FID in one experiment and by GC–FID in the other two experiments, noting that both FT-IR and GC–FID have relatively low sensitivity for acetaldehyde. Figure 4 illustrates the spectra obtained from the irradiated CH₃ONO–NO–2,3dimethylpentanal–air mixture with 31% of the initial 2.35×10^{14} molecule cm⁻³ of 2,3-dimethylpentanal reacting after a total irradiation time of 18 min, and with corresponding amounts (in units of 10¹³ molecule cm⁻³) of 2-butanone, 3-methyl-2-pentanone, and acetaldehyde of 1.75, 0.44, and 4.82, respectively, being formed.

The products also react with OH radicals, and their secondary reactions were taken into account as described previously [28], using the rate constants measured here for 2,3-dimethylpentanal and 3-methyl-2-pentanone and the recommended values [27] for acetaldehyde and 2-butanone. Corrections for secondary reactions were <1% for 2-butanone, <5% for 3-methyl-2-pentanone, and <11% for acetaldehyde. Plots of the amounts of acetaldehyde, 2-butanone,



Figure 4 Infrared spectra from a CH₃ONO–NO– 2,3-dimethylpentanal–air irradiation (concentrations are in molecule cm⁻³). (A) Initial 2,3-dimethylpentanal (2.35 × 10¹⁴). (B) Irradiated mixture, with 31% of 2,3dimethylpentanal reacted, after subtraction of unreacted CH₃ONO and its photolysis products in the presence of NO. (C) From (B) after subtraction of unreacted 2,3dimethylpentanal and its known carbonyl products acetaldehyde, 2-butanone, and 3-methyl-2-pentanone (see text). Peaks marked with + and * are attributed to the products RONO₂ and RC(O)OONO₂, respectively. (D) CH₃CHO reference (4.92 × 10¹³). (E) 2-Butanone reference (2.46 × 10¹³). (F) 3-Methyl-2-pentanone reference (2.46 × 10¹³).

and 3-methyl-2-pentanone formed, corrected for reaction with OH radicals, against the amounts of 2,3dimethylpentanal reacted with OH radicals are shown in Figs. 5 (acetaldehyde and 2-butanone) and 6 (3methyl-2-pentanone). The formation yields of acetaldehyde and 2-butanone decrease with increasing extent of reaction (see the Discussion section), and were uniformly lower during the two experiments with 2-methylpropene present. This behavior suggests that at least part of the acetaldehyde and 2-butanone observed arise from reactions involving an acylperoxy radical precursor(s) (see later and Atkinson and Aschmann [29]). In contrast, the plot (Fig. 6) for 3methyl-2-pentanone is a good straight line with no evidence for curvature, and hence no evidence for the intermediary of an acylperoxy radical. The formation yields for 3-methyl-2-pentanone and (based on the initial slopes obtained from a second-order regression) for acetaldehyde and 2-butanone are given in Table II.

The residual IR spectra (see Fig. 4C) showed a set of absorption bands at 795, 1299, 1736, and 1825 cm^{-1} and another set at 856, 1284, and 1651 cm⁻¹, which can be attributed to the generalized products RC(O)OONO₂ and RONO₂, respectively. After the first 8-min irradiation period in the experiment



Figure 5 Plots of the amounts of acetaldehyde and 2butanone formed (corrected for secondary reactions, see text) against the amounts of 2,3-dimethylpentanal reacted with the OH radical. (\triangle , \Box) Experiments with 2-methylpropene present, analyses of acetaldehyde and 2-butanone by GC– FID. (\bigcirc , \bullet) Experiment with no 2-methylpropene present, analyses of products by (\bigcirc) GC–FID and (\bullet) in situ FT-IR spectroscopy. The lines are from second-order regressions (for acetaldehyde using only the FT-IR data in the experiment without 2-methylpropene).

Table IIProducts Observed, and Their Molar Yields,from the Reaction of OH Radicals with2,3-Dimethylpentanal in the Presence of NO

Product ^a	Molar Yield	Molar Yield at First Data Point ^b
Acetaldehyde	$0.98^{b,c}$ $0.80^{c,d}$	0.82
2-Butanone	$0.27^{b,c}$ $0.25^{c,d}$	0.26
3-Methyl-2- pentanone	0.054 ± 0.010^{e}	0.054 ± 0.010
$\hat{RC}(O)OONO_2$		0.28
RONO ₂	0.12 ± 0.04^b	0.12 ± 0.04

^{*a*} 2,3-Dimethylpentanal, organic nitrates (RONO₂), acylperoxy nitrates (RC(O)OONO₂), and, in the experiments without 2-methylpropene, acetaldehyde were measured by FT-IR spectroscopy, and acetaldehyde, 2-butanone, and 3-methyl-2-butanone were measured by GC–FID. The measured concentrations of acetaldehyde, 2-butanone, and 3-methyl-2-butanone have been corrected for secondary reactions with OH radicals (see text).

- ^b Experiment without 2-methylpropene present (see text).
- ^c Initial slope of second-order regression (Fig. 5).
- ^{*d*} Experiments with 2-methylpropene present.

^e From all three experiments. Indicated error is two leastsquares standard deviations of the plot shown in Fig. 6 combined with estimated overall uncertainties in the FT-IR analyses for 2,3dimethylpentanal of $\pm 15\%$ and in the GC–FID response factor for 3-methyl-2-pentanone of $\pm 5\%$.



Figure 6 Plot of the amounts of 3-methyl-2-pentanone formed (corrected for secondary reactions, see text) against the amounts of 2,3-dimethylpentanal reacted with the OH radical. Analysis of 3-methyl-2-pentanone by GC–FID and of 2,3-dimethylpentanal by in situ FT-IR spectroscopy. Symbols are as in Fig. 5.

without 2-methylpropene, which consumed $\sim 17\%$ of the initial 2.35×10^{14} molecule cm⁻³ of 2,3dimethylpentanal, the remaining NO ($\sim 1.0 \times 10^{14}$ molecule cm⁻³) was sufficiently high that the thermal decay of RC(O)OONO₂ [1,2] during an ensuing 69-min dark period caused spectral differences that allowed separate spectra to be "synthesized" for the RC(O)OONO₂ and RONO₂ species. On the basis of the derived spectra and the common integrated absorption coefficient applicable to the bands at $\sim 1290 \text{ cm}^{-1}$ [30], the concentrations of RONO2 were calculated for the three irradiation periods of this experiment and resulted in an estimated yield of $12 \pm 4\%$ for RONO₂. The yield of RC(O)OONO₂ for the first irradiation period was estimated as $\sim 28\%$, but its concentration could not be followed meaningfully for the other irradiation periods because of its thermal decay.

DISCUSSION

H-Atom Abstraction from 1,4-Cyclohexadiene and 1,3,5-Cycloheptatriene

In agreement with the previous study of Ohta [16], we observed benzene to be formed from the reaction of OH radicals with 1,4-cyclohexadiene, and our benzene formation yield of $12.5 \pm 1.2\%$ (weighted average, two standard deviation) is in reasonable agreement with those of Ohta [16] of $15.4 \pm 0.3\%$ from CH₃ONO-1,4-cyclohexadiene-N₂-O₂ (with ≥ 100 Torr of O₂) irradiations and $15.1 \pm 0.3\%$ from

 $H_2O_2-1,4$ -cyclohexadiene $-N_2-O_2$ irradiations (both at a total pressure of one atmosphere). As discussed by Ohta [16], benzene formation is consistent with direct H-atom abstraction by O₂ from the cyclohexadienyl radical, as shown in Scheme 1. Formation of benzene could also arise after addition of O₂ to the cyclohexadienyl radical to form the C₆H₇O₂• radical, followed by elimination of HO₂ (also shown in Scheme 1). H-atom abstraction from the allylic C-H bonds in 1,4-cyclohexadiene therefore accounts for 12-15% of the overall OH radical reaction, with the remainder proceeding by OH radical addition to form the 1-hydroxycyclohex-4-en-2-yl radical. The C-H bond dissociation energy of the allylic C-H bonds in 1,4-cyclohexadiene is 76.3 kcal mol^{-1} , based on the heats of formation of 1,4-cyclohexadiene [31] and the cyclohexadienyl radical [31,32].

The C–H bond dissociation energy of the allylic C–H bonds in cycloheptatriene is similar, being in the range 73.2 [31,33] to 75.6 kcal mol⁻¹ [31,34], yet we observed no formation of tropone (<1.2%) from the reactions shown in Scheme 2, nor of benzaldehyde (<0.7%) (the product arising after any isomerization of tropyl radicals to benzyl radicals [2]). Clearly, either H-atom abstraction is negligible (<2%) or the expected cycloalkoxy radical (A in Scheme 2) must decompose rather than reacting with O₂. By analogy with the HOCH₂C(CH₃)=CHCH₂O[•] radical formed from the reaction of OH radicals with isoprene [35,36], decomposition of the cycloalkoxy radical (A) to form the conjugated vinyl radical HC(O)CH=CHCH=CHCH=C[•]H is



Scheme 1



Scheme 2

expected to be slow. It therefore appears that for 1,3,5-cycloheptatriene H-atom abstraction is of no importance.

H-Atom Abstraction from the 2-Position CH Group in 2,3-Dimethylpentanal

The reaction of OH radicals with 2,3-dimethylpentanal proceeds by H-atom abstraction from the various C-H bonds, with H-atom abstraction from the C-H bond in the CHO group being predicted to be dominant and H-atom abstraction from the C-H bonds in the three CH₃ groups being minor [3]. Schemes 3–6 show predicted reaction schemes after H-atom abstraction from the C–H bonds at the CHO group, the 2-position CH group, the 3-position CH group, and the 4-position CH₂ group, respectively, where a bold arrow indicates a predicted dominant pathway (by a factor of 5) and a dashed arrow indicates a pathway predicted to account for <4% of the overall alkoxy radical reaction rate (the rates of the various alkoxy radical reactions were estimated as described by Atkinson [4,24] and Aschmann et al. [25] using thermochemical data from the NIST program [31] and IUPAC [27]).

Schemes 3-6 show that the expected products are acetaldehyde plus 2-butanone or 3 molecules of acetaldehyde after H-atom abstraction from the CHO group, 3-methyl-2-pentanone after H-atom abstraction from the 2-position CH group, 2-butanone plus acetaldehyde after H-atom abstraction from the 3-position CH group, and 3 molecules of acetaldehyde after H-atom abstraction from the 4-position CH₂ group. Acyl peroxy radicals, RC(O)OO[•], occur as intermediates after H-atom abstraction from the CHO group (Scheme 3) and, if an alkoxy radical isomerization occurs, after H-atom abstraction from the 4-position CH₂ group (Scheme 6). The intermediary of these acyl peroxy radicals (forming acyl peroxynitrates $RC(O)OONO_2$ as a temporary "reservoir" species which, as noted above, were observed by FT-IR spectroscopy) accounts for the decreasing yield of acetaldehyde and 2-butanone with increasing extent of reaction. This occurs [29] because the NO₂/NO concentration ratio increases as the reaction proceeds (from photolysis of methyl nitrite which has an overall reaction of CH₃ONO + $h\nu$ $(+O_2) \rightarrow HCHO + OH + NO_2$ and from conversion of NO to NO₂ by HO₂ and organic peroxy radicals [1]), leading to a longer effective lifetime of the RC(O)OONO2 species. Furthermore, more rapid NO to NO₂ conversion would occur in the experiments with 2-methylpropene present because of the higher reactivity of 2-methylpropene and the higher organic/NO_x ratio, leading to a higher fraction of the OH radicals reacting with organic compounds in competition with reaction with NO and NO₂. In contrast, no acyl peroxy radical intermediate is involved in the formation of 3-methyl-2-pentanone in Scheme 4.

Therefore, 3-methyl-2-pentanone appears to be the sole product formed after initial H-atom abstraction from the 2-position CH group. Formation of 3-methyl-2-pentanone after initial H-atom abstraction from the CHO group (Scheme 3) is predicted [24,25] to account for $\leq 3\%$ of the products of this pathway and involves the intermediary of an acyl peroxy radical. As noted above, we observe no evidence for an acyl peroxy radical intermediate in the formation of 3-methyl-2-pentanone (Fig. 6). Our measured 3-methyl-2-pentanone formation yield of $5.4 \pm 1.0\%$ (plus any formation of the organic nitrate CH₃CH₂CH(CH₃)C(ONO₂)(CH₃)CHO; see Scheme 6) is therefore the percentage of the overall OH radical reaction with 2,3-dimethylpentanal proceeding by H-atom abstraction from the 2-position CH group.

The product yields given in Table II indicate that at the first measurement time in the experiment without added 2-methylpropene $\sim 90\%$ of the reaction products and pathways are accounted for, assuming that





Scheme 5

acetaldehyde is a co-product to the 2-butanone formed after H-atom abstraction from the CHO group and the 3-position CH group, and that three molecules of acetaldehyde are formed after H-atom abstraction from the CHO group (the alternate products being 2-butanone plus acetaldehyde) and from the 4-position CH₂ group as shown in Schemes 3, 5 and 6).

The estimation method of Kwok and Atkinson [3] predicts that the percentages of the overall OH radical reaction proceeding by H-atom abstraction are from

the CHO group, 61%; from the 2-position CH group, 5.3%; from the 3-position CH group, 27%; from the 4-position CH₂ group, 3.4%; and from the three CH₃ groups, 3% (total); and with an overall OH radical reaction rate constant of 3.4×10^{-11} cm³ molecule⁻¹ s⁻¹ at 298 K. The predicted total OH radical reaction rate constant agrees well with our measured value of $(4.2 \pm 0.7) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, and the predicted percentage of the overall reaction occurring at the 2-position CH group (5.3%) agrees very



well with the measured percentage of 5.4 \pm 1.0%. Unfortunately, the same products (2 butanone and/or acetaldehyde) are formed after H-atom abstraction from the CHO, 3-position CH, and 4-position CH₂ groups and hence our product data shed no light on the relative importance of these three H-atom abstraction pathways. Until such data become available, in particular confirming or disproving the prediction of the Kwok and Atkinson [3] estimation method that for aldehydes H-atom abstraction from the CH or CH2 groups located two carbon atoms away from the CHO group (i.e., the 3-position CH group in 2,3-dimethylpentanal) is significantly enhanced over adjacent CH or CH2 groups, then the Kwok and Atkinson [3] estimation method appears to offer an approximate means of estimating the relative importance of H-atom abstraction from the various CH, CH₂, and CH₃ groups in aliphatic aldehydes.

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