β-Ionone Reactions with the Nitrate Radical: Rate Constant and Gas-Phase Products

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ABSTRACT: The bimolecular rate constant of $k_{NO_3\bullet+\beta\text{-ionone}}$ ($9.4 \pm 2.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} was measured using the relative rate technique for the reaction of the nitrate radical ($NO_3\bullet$) with 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (β-ionone) at (297 ± 3) K and 1 atmosphere total pressure. In addition, the products of β-ionone + $NO_3\bullet$ reaction were also investigated. The identified reaction products were glyoxal (HC(=O)C(=O)H), and methylglyoxal ($CH_3C(=O)C(=O)H$). Derivatizing agents O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine and N,O-bis(trimethylsilyl)trifluoroacetamide were used to propose the other major reaction products: 3-oxobutane-1,2-diyl nitrate, 2,6,6-trimethylcyclohex-1-ene-carbaldehyde, 2-oxo-1-(2,6,6-trimethylcyclohex-1-en-1-yl)ethyl nitrate, pentane-2,4-dione, 3-oxo-1-(2,6,6-trimethylcyclohex-1-en-1-yl)butane-1,2-diyl dinitrate, 3,3-dimethylcyclohexane-1,2-dione, and 4-oxopent-2-enal. The elucidation of these products was facilitated by mass spectrometry of the derivatized reaction products coupled with plausible β-ionone + $NO_3\bullet$ reaction mechanisms based on previously published volatile organic compound + $NO_3\bullet$ gas-phase mechanisms. The additional gas-phase products 5-acetyl-2-ethylidene-3-methylcyclopentyl nitrate, 1-(1-hydroxy-7,7-dimethyl-2,3,4,5,6,7-hexahydro-1H-inden-2-yl)ethanone, 1-(1-hydroxy-3*a*,7-dimethyl-2,3,3*a*,4,5,6,-hexahydro-1H-inden-2-yl)ethanone, and 5-acetyl-2-ethylidene-3-methylcyclopentanone are proposed to be the result of cyclization through a reaction intermediate. © 2009 Wiley Periodicals, Inc.* Int J Chem Kinet 41: 629–641, 2009

INTRODUCTION

Recently, the American Academy of Allergy, Asthma & Immunology [1] issued a report that states that approximately 15% (1 in 7) cases of asthma are work related, resulting in ~24.5 million missed workdays annually. Unfortunately, the direct causes of many of these work-related asthma (WRA) cases are still unknown; although research efforts have indicated that volatile organic compounds (VOCs) and their oxidation products may be partially responsible [2]. Several studies have been conducted on VOCs and their specific health effects in the indoor environment; however, the presence of individual VOCs does not completely explain elevated irritation levels [3,4]. These

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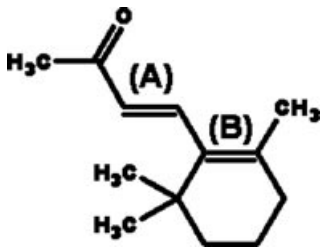
levels may be attributed to the formation of yet unknown products generated from oxidation reactions between unsaturated VOCs and indoor oxidants such as OH• (hydroxyl radical), O_3 (ozone), and NO_3• (nitrate radical).

The chemistry of the NO_3• with a number of VOCs and semi-VOCs, which can be found both outdoors and indoors, has been well studied [5–9]. In the indoor environment, these types of reactions can occur quickly compared with a typical air exchange of 0.6 h^{-1} [10]. For example, NO_3• (given the estimated indoor [NO_3•] = 1 part per trillion [ppt]) [11,12] reactions with terpinolene and α-terpinene (found in pine oil cleaners) can occur 14 and 27 times faster, respectively, than they can be removed by a typical building air exchange [10]. Consequently, these types of reactions generate a number of indoor oxygenated products such as aldehydes, ketones, dicarbonyls (e.g., glyoxal, methylglyoxal, 4-oxopentanal), and organic nitrates, (e.g., alkyl nitrates, peroxyacyl nitrates [PANs], hydroxynitrates, dinitrates) [5,13,14]. Furthermore, NO_3• reactions have been shown to irreversibly damage amino acids by transformation into β-nitrate esters, β-carbonyl compounds, and/or aromatic nitro compounds [15]. All of these oxygenated organic compounds have the potential to induce a respiratory response, including WRA. Organic nitrates may also have the potential to be carcinogenic. For example, polyaromatic hydrocarbons (PAHs) react with nitrate radicals to form nitro-PAHS. Several nitro-PAHS (e.g., 6-nitrobenzo[*a*]pyrene, 3-nitroperylene, 1-nitropyrene, and 6-nitrochysene) have been identified as mutagens and carcinogens [16].

Room deodorization introduces a number of VOCs and semi-VOCs into the indoor environment. One such compound used in deodorizing consumer products is β-ionone (4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one) (Structure 1), a component of the violet scent. Worldwide usage has been estimated at 100 to 1000 metric tons annually [17]. In the work presented here, the β-ionone + NO_3• rate constant has been measured using the relative rate method. Some of the products of this reaction are also reported. Neither the NO_3• rate constant nor the respective reaction mechanisms for β-ionone + NO_3• have been reported previously.



Structure 1

EXPERIMENTAL

Apparatus and Materials

Experiments to measure the gas-phase rate constant of the NO_3• + 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (β-ionone, Structure 1) reaction were conducted with a previously described apparatus [18,19]. A brief description is provided here. Reactants were introduced and samples were withdrawn through a 6.4-mm Teflon® Swagelok fitting attached to a 65-L Teflon® film chamber. Compressed air from the National Institute for Occupational Safety and Health (NIOSH) facility was passed through anhydrous $CaSO_4$ (Drierite, Xenia, OH) and molecular sieves (Drierite, Xenia, OH) to remove both moisture and organic contaminants. This dry compressed air was added as a diluent to the reaction chambers and measured with a 0–100 L min^{-1} mass flow controller (MKS Instruments, Inc., Andover, MA). Analysis of this treated compressed air by gas chromatography/mass spectrometry revealed that if contaminants were present, they would be below the ppt range. The treated compressed air was also analyzed for nitric oxide (NO) with a Thermo Electron Model 42i NO-NO_2-NO_x analyzer (Thermo Fisher Scientific, Inc., Waltham, MA). The filler system was equipped with a syringe injection port facilitating the introduction of both liquid and gaseous reactants into the chambers with the flowing airstream. All reactant mixtures and calibration standards were generated by this system.

All reaction kinetic samples were quantitatively monitored using an Agilent 6890 gas chromatograph (Agilent Technologies, Palo Alto, CA) with a 5973 mass selective detector (GC/MS) and Agilent ChemStation software. Gas samples were cryogenically collected employing an Entech 7100 sampling system (Entech Instruments, Inc., Simi Valley, CA) utilizing the following trap and temperature parameters: 50 mL of chamber contents were collected onto trap 1 (packed silanized glass beads) at −150°C. After sample collection, trap 1 was heated to 230°C and the sample transferred under a flow of ultrahigh purity helium (UHP He) onto trap 2 (packed silanized glass beads) cooled to −30°C. trap 2 was then heated to 180°C and the sample was transferred under a UHP He flow onto trap 3, a silanized 0.53-mm i.d. tube cooled to −160°C, which was subsequently heated to 220°C to inject the sample

onto an Rtx-VRX (Restek, Bellefonte, PA) GC column (0.25-mm i.d., 30-m length, and 1.4-μm film thickness). These series of cryogenic trap manipulations reduced the background water level, ensured consistency of replicate samples, and improved the chromatograph peak shapes. The reduction in background water levels is accomplished by gentle heating (40°C) with helium flow on each of the traps along with careful timing of cooling the next trap for collection. The GC temperature program used was as follows: initial temperature of 45°C held for 8 min after sample injection and then increased 10°C/min to 220°C and held for 4 min. The Agilent 5973 mass selective detector was tuned using perfluorotributylamine (FC-43). Full-scan electron impact (EI) ionization spectra were collected from $m/z = 35$ to $m/z = 650$. Preliminary compound identifications from the Agilent 6890/5973 GC/MS data sets were made by searching the NIST 98 Mass Spectral Library.

The identification of reaction products was made using *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) to derivatize carbonyl products, whereas alcohols were derivatized using *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) [20]. Possible carboxylic acids, ketal-alcohols, and aldehydic-alcohols were derivatized using a combination of PFBHA and BSTFA. Experimental methods for reaction product identification were similar to methods used for kinetic experiments, except that the reference compound was excluded from the reaction mixture. An additional port was added to the Teflon chamber to facilitate the injection of N_2O_5 (described in the following text).

Derivatized reaction products were analyzed using a Varian (Varian, Inc., Palo Alto, CA) 3800/Saturn 2000 GC/MS system operated in both the EI and CI modes [20]. Compound separation was achieved by a J&W Scientific (Folsom, CA) DB-5MS (0.32-mm i.d., 30-m length, 1-μm film thickness) column and the following GC oven parameters: 60°C for 1 min, then 20°C/min to 170°C, then 3°C/min to 280°C, and held for 5 min.

Samples were injected in the splitless mode, and the GC injector was returned to split mode 1 min after sample injection, with the following injector temperature parameters: 60°C for 1 min, then 180°C/min to 250°C, and held to the end of the chromatographic run [20]. The Saturn 2000 ion trap mass spectrometer was tuned using FC-43. Full-scan EI ionization spectra were collected from $m/z = 40$ to $m/z = 650$. Acetonitrile was the chemical ionization (CI) reagent used for all CI spectra. When possible, commercially available samples of the identified products were derivatized and subsequently analyzed to verify matching ion spectra and chromatographic retention times.

Nitrate radicals were generated by the thermal decomposition of N_2O_5 using a similar method as described by Atkinson et al. [21,22] N_2O_5 (solid) kept at −85°C was heated and allowed to transfer to an evacuated 2-L collection bottle until pressure was between 0.1 and 0.6 Torr. The collection bottle was then pressurized with UHP nitrogen up to 1000 Torr and connected to the reaction chamber via a Teflon® shutoff valve. The valve to the collection bottle and the chamber shutoff valve were opened and the system was allowed to equilibrate for 10 s. For kinetics and product experiments, approximately 10 min elapsed before any samples were collected after the introduction of N_2O_5.

All compounds were used as received and had the following purities: from Sigma-Aldrich (Milwaukee, WI): limonene (99%), 2-carene (97%), 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (β-ionone) (95%), acetonitrile (99.93%), BSTFA (99%), PFBHA (98+%), and methanol (99%). Nitrogen dioxide as a 5% mixture in nitrogen and UHP oxygen were obtained from Butler Gases (Morrisville, PA). Helium (UHP grade), the carrier gas, was supplied by Amerigas (Sabraton, WV) and used as received. Experiments were carried out at 297 ± 3 K and at a pressure of 1 atm.

Methods

The experimental procedures for determining the β-ionone + NO_3• reaction kinetics were similar to those described previously [18,19].

$$\beta\text{-Ionone} + NO_3\bullet \xrightarrow{k_{NO_3\cdot+\beta\text{-ionone}}} \text{Products} \quad (1)$$

$$\text{Reference} + NO_3\bullet \xrightarrow{k_{Ref}} \text{Products} \quad (2)$$

The rate equations for reactions (1) and (2) are combined and integrated, resulting in the following equation:

$$\ln\left(\frac{[\beta\text{-ionone}]_0}{[\beta\text{-ionone}]_t}\right) = \frac{k_{NO_3\cdot+\beta\text{-ionone}}}{k_{Ref}} \ln\left(\frac{[Ref]_0}{[Ref]_t}\right) \quad (3)$$

If the reaction with NO_3• is the only removal mechanism for β-ionone and the reference compound, a plot of $\ln([\beta\text{-ionone}]_0/[\beta\text{-ionone}]_t)$ versus $\ln([Ref]_0/[Ref]_t)$ yields a straight line with an intercept of zero. Multiplying the slope of this linear plot by k_{Ref} yields $k_{NO_3\cdot+\beta\text{-ionone}}$ (Fig. 1). The NO_3• rate constant experiments for β-ionone employed the use of two reference compounds: 2-carene and limonene. The use of two different reference compounds with different NO_3• rate constants strengthens the accuracy of the β-ionone/NO_3• rate constant measurement and demonstrates that other reactions are not removing β-ionone.

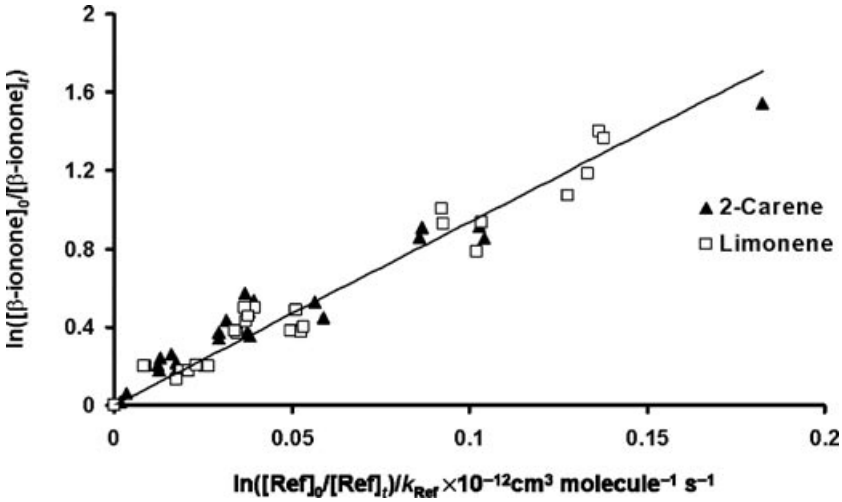


Figure 1 4-(2,6,6-Trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (β-ionone) relative rate plot with 2-carene (▲) and limonene (□) as reference compounds. The $NO_3\bullet$ + β-ionone rate constant, $k_{NO_3\cdot+\beta\text{-ionone}}$, was measured to be $(9.4 \pm 0.2) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

For the β-ionone/$NO_3\bullet$ kinetic experiments, the typical concentrations of the pertinent species in the 65-L Teflon chamber were 1.1–5.6 ppm (2.7–13.8×10^{13} molecule cm^{-3}) β-ionone, 0.3–0.8 ppm (0.7–2.0 $\times$ 10^{13} molecule cm^{-3}) reference, 0.1–0.6 Torr of N_2O_5 (3.9–23 ppm, which corresponds to an $NO_3\bullet$ concentration of 0.3–1.5 ppm at 298 K) [23], and 6 ppb (1.4×10^{11} molecule cm^{-3}) NO as background in NIOSH air. The gas-phase mixtures were allowed to reach equilibrium before initial species concentration ($[X]_0$) samples were collected. The total ion chromatogram (TIC) from the Agilent 5973 mass selective detector was used to determine β-ionone and reference concentrations.

Derivatization of the carbonyl reaction products was initiated by flowing 15–25 L of chamber contents at 3.8 L min^{-1} through an impinger containing 4 mL of acetonitrile and 250 μL of PFBHA (0.02 M) in acetonitrile to derivatize the carbonyl reaction products to oximes [20], with no effort to prevent acetonitrile evaporation during sample collection. The sample was removed from the impinger and allowed to react for a 24- to 48-h time period in the dark. The reacted solutions were gently blown to dryness with UHP N_2, reconstituted with 100 μL of methanol, and then 1 μL of the reconstituted solution was injected onto the Varian 3800/Saturn 2000 GC/MS system. The derivatization of hydroxy groups (alcohols) was achieved by subsequent reconstitution of the dried PFBHA oximes by the addition of 150 μL of commercially available BSTFA. These PFBHA/BSTFA solutions were heated to approximately 60°C for 45 min to complete the silylation, and then 1 μL of the solution was injected into the Varian 3800/Saturn 2000 GC/MS system [18].

RESULTS

β-Ionone/$NO_3\bullet$ Reaction Rate Constant

The $NO_3\bullet$ rate constant for (β-ionone, Structure 1) was obtained using the relative rate method described above. The plot of a modified version of Eq. (3) is shown in Fig. 1. The $\ln([Ref]_0/[Ref]_t)$ term is divided by the respective reference rate constant (2-carene (19 ± 5) $\times$ 10^{-12} cm^3 molecule^{-1} s^{-1} and limonene (12.2 ± 3.1) $\times$ 10^{-12} cm^3 molecule^{-1} s^{-1}) [24] and multiplied by 10^{-12} cm^3 molecule^{-1} s^{-1}, resulting in a unitless number. This yields a slope that is equal to the $NO_3\bullet$/β-ionone rate constant, $k_{NO_3\cdot+\beta\text{-ionone}}$, *divided by* 10^{-12} cm^3 molecule^{-1} s^{-1}. This modification allows for a direct comparison of the two reference compound/β-ionone data sets. The slope of the line shown in Fig. 1 yields an $NO_3\bullet$ bimolecular rate constant, $k_{NO_3\cdot+\beta\text{-ionone}}$, of $(9.4 \pm 0.2) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The use of 2-carene and limonene as references resulted in $NO_3 \cdot +\beta$-ionone bimolecular rate constants of $(9.3 \pm 0.3) \times 10^{-12}$ and (9.4 ± 0.2) $\times$ 10^{-12} cm^3 $\times$ 10^{-12} molecule^{-1} s^{-1}, respectively. The data points at the origin are experimental points before $NO_3\bullet$ addition, $t = 0$; data showed no detectable loss of β-ionone or reference. The error in the rate constant is the 95% confidence interval from the random uncertainty in the slope. Incorporating the uncertainties associated with the reference rate constants (±25% for 2-carene and limonene) used to derive the β-ionone/$NO_3\bullet$ rate constant yields a final value of (9.4 ± 2.4) $\times$ 10^{-12} cm^3 molecule^{-1} s^{-1} for $k_{NO_3\cdot+\beta\text{-ionone}}$ [24]. The β-ionone/$NO_3\bullet$ rate constant, $k_{NO_3\cdot+\beta\text{-ionone}}$, has not been previously

reported. The ratios $k_{NO_3\cdot+\beta\text{-ionone}}/k_{NO_3\cdot+2\text{-carene}}$ and $k_{NO_3\cdot+\beta\text{-ionone}}/k_{NO_3\cdot+\text{limonene}}$ incorporating the uncertainties are 0.5 ± 0.1 and 0.8 ± 0.2, respectively.

β-Ionone/NO_3• Reaction Products

The products observed from the β-ionone/NO_3• reaction (hydrogen abstraction or NO_3• addition to carbon-carbon double bonds) are listed in Table I. The β-ionone/NO_3• reaction products observed and positively identified using the pure compound for verification by derivatization were glyoxal (HC(=O)C(=O)H) and methylglyoxal ($CH_3C(=O)C(=O)H$). Structures and ions (expected CI vs. observed CI) used to identify these compounds are listed in Table I. Elucidation of the other major proposed reaction products (also listed in Table I) were facilitated by mass spectrometry of the derivatized reaction product coupled with plausible β-ionone/NO_3• reaction mechanisms on the basis of previously published VOC/NO_3• gas-phase reaction as described in the following text [5,12,24–27].

The derivatization of nonsymmetric carbonyls using PFBHA or PFBHA/BSTFA typically resulted in multiple chromatographic peaks due to stereoisomers of the oximes. The identification of multiple peaks of the same oxime compound is relatively simple since the mass spectra for each chromatographic peak of a particular oxime are almost identical [20]. In most cases, the $m/z = 181$ ion relative intensity for the chromatographic peaks due to β-ionone + NO_3• reaction product oximes was the base peak in the mass spectrum and was used to generate selected ion chromatograms. The mass spectra of compounds that were additionally derivatized with BSTFA contained $m/z = 73$ ions from the $[Si(CH_3)_3]^+$ fragments. A chromatogram displaying the latter portion of the GC run (29–44 min) in which organic nitrate products were observed is shown in Fig. 2. The product data are described in the following text.

The following chronological chromatographic retention time results and mass spectra data were observed utilizing PFBHA or PFBHA/BSTFA derivatization and the Varian 3800/Saturn 2000 GC/MS system. The reaction products' chromatographic peak areas were a function of the initial β-ionone concentration and were observed only after NO_3• initiation of β-ionone/methanol/air mixtures. Derivatization experiments performed in the absence of β-ionone, but in the presence of all other chemicals in the reaction chamber (NO_3•/air/methanol), did not result in any of the data reported in the subsequent text except for small amounts (as noted by chromatographic peak areas) of methylglyoxal and glyoxal. However, the glyoxal and methylglyoxal oxime peak areas increased significantly by a factor of 5 and 16, respectively, with β-ionone + NO_3•, indicating that methylglyoxal and glyoxal are likely products of the reaction.

Oxime at Retention Time 11.4 min

The oxime observed with a chromatographic retention time of 11.4 min had ions of m/z (relative intensity): 59 (7%), 161 (6%), 181 (100%), 195 (5%), and 280 (5%–10%). Using acetonitrile for CI, an M + 1 ion of $m/z = 298$ was observed for the PFBHA-derivatized sample. A proposed reaction product assignment of 3-oxobutane-1,2-diyl dinitrate was based on observed data.

Oxime at Retention Time 20.8 min

The oxime observed with a chromatographic retention time of 20.8 min had ions of m/z (relative intensity): 91 (30%), 105 (22%), 117 (25%), 132 (40%), 148 (100%), 181 (85%), and 330 (30%). In the CI spectra, an M + 1 ion of $m/z = 346$ was observed for the PFBHA-derivatized sample. A proposed reaction product assignment of 5-acetyl-2-ethylidene-3-methylcyclopentyl nitrate was based on observed data.

Oxime at Retention Time 21.1 min

The oxime with a chromatographic retention time of 21.1 min had ions of m/z (relative intensity): 96 (30%), 150 (58%), 166 (100%), 181 (90%) 347 (17%), and 429 (44%). In the CI spectra, an M + 1 ion of $m/z = 348$ was observed for the PFBHA-derivatized sample. A proposed reaction product assignment of 2,6,6-trimethylcyclohex-1-ene-1-carbaldehyde was based on observed data.

Glyoxal (HC(=O)C(=O)H)

The chromatographic peaks for the oxime observed at 24.1 and 24.4 min have been described previously [18,28].

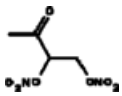
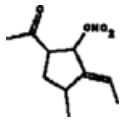
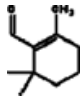
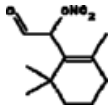
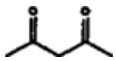
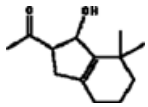
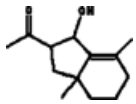
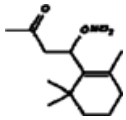
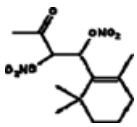
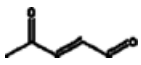
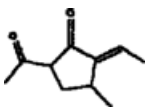
Methylglyoxal ($CH_3C(=O)C(=O)H$)

The chromatographic peaks for the oxime observed at 23.4, 24.5, and 25.5 min have been described previously [18,28].

Oxime at Retention Times 25.7, 26.6, and 27.2 min

The oxime observed at retention times of 25.7, 26.6, and 27.2 min had ions of m/z (relative intensity): 122 (35%), 150 (100%) 181 (55%), and 331 (35%). In the

Table I Proposed β-Ionone/NO_3• Reaction Products

Retention Time (min)	Name	Molecular Weight (amu)	Structure	CI Ions Expected	CI Ions Observed
11.4	3-Oxobutane-1,2-diyl dinitrate	194		390	298
20.8	(2*E*)-5-Acetyl-2-ethylidene-3-methylcyclopentyl nitrate	213		409	346
21.1	2,6,6-Trimethylcyclohex-1-ene-1-carbaldehyde[a]	152		348	348
24.1 24.4	Glyoxal[a]	58		449	449
23.4 24.5 25.5	Methylglyoxal[a]	72		463	463
25.7 26.6 27.2	2-Oxo-1-(2,6,6-trimethylcyclohex-1-en-1-yl)ethyl nitrate	227		423	360
29.3	Pentane-2,4-dione	100		491	491
29.6 31.2	1-(1-Hydroxy-7,7-dimethyl-2,3,4,5,6,7-hexahydro-1*H*-inden-2-yl)ethanone[a]	208		404	404
29.9 32.8	1-(1-Hydroxy-3*a*,7-dimethyl-2,3,3*a*,4,5,6-hexahydro-1*H*-inden-2-yl)ethanone[a]	208		404	404
31.5	3-Oxo-1-(2,6,6-trimethylcyclohex-1-en-1-yl)butyl nitrate	255		451	386
31.9 33.3	3-Oxo-1-(2,6,6-trimethylcyclohex-1-en-1-yl)butane-1,2-diyl dinitrate	316		512	418
35.5	3,3-Dimethylcyclohexane-1,2-dione	140		531	531
39.6 41.1 41.5 43.1	(2*E*)-4-Oxopent-2-enal[a]	98		489	No CI ions
42.4	(2*E*)-5-Acetyl-2-ethylidene-3-methylcyclopentanone	166		557	557

[a] Products previously observed with β-ionone/OH and β-ionone/O_3 (Forester et al. [28]).

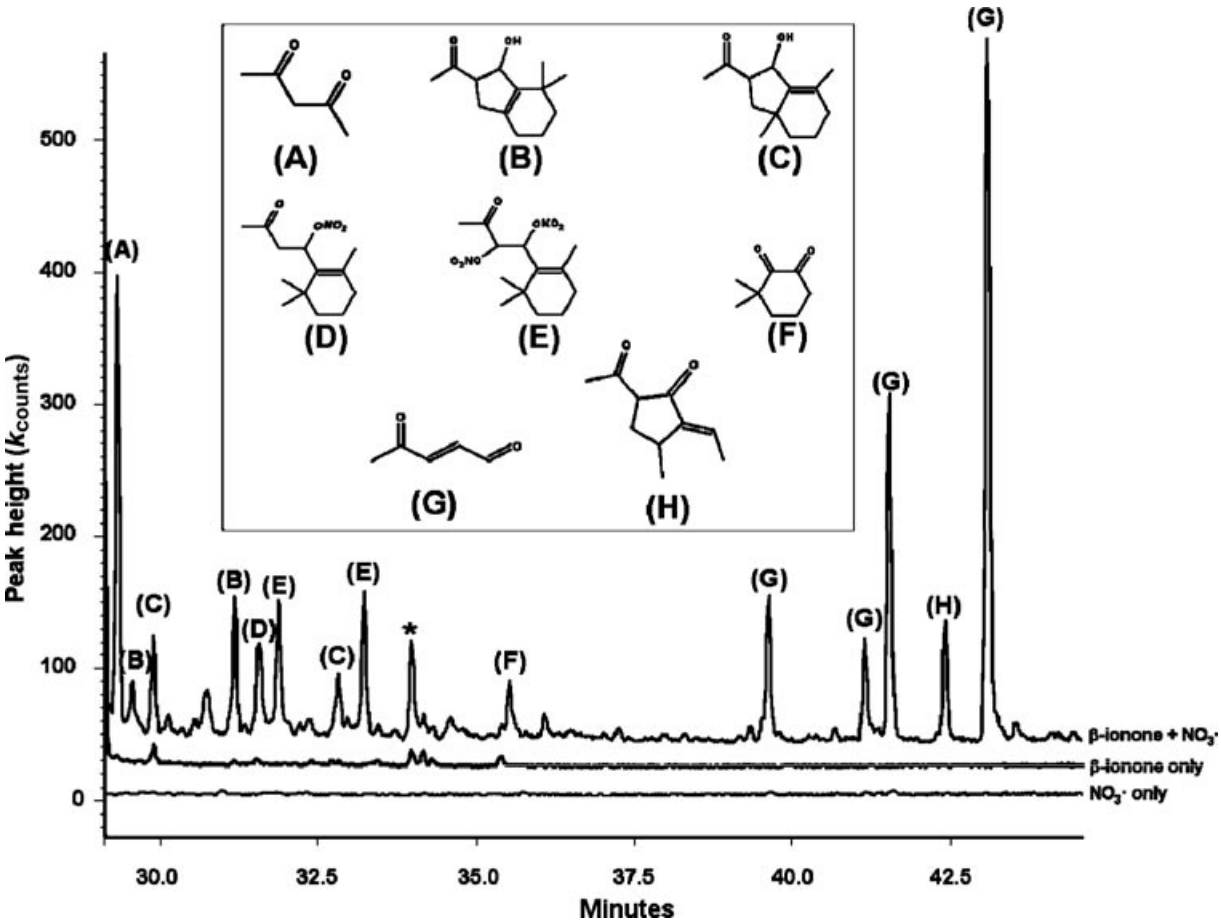


Figure 2 Overlaid chromatograms of β-ionone only, NO_3• only, and β-ionone + NO_3• in the reaction chamber. Data were offset for clarity. * indicates β-ionone/NO_2 product.

CI spectra, an M + 1 ion of $m/z = 360$ was observed. A proposed reaction product assignment of 2-oxo-1-(2,6,6-trimethylcyclohex-1-en-1-yl)ethyl nitrate was based on observed data.

Oxime at Retention Times of 29.3 min

The oxime observed at a retention time of 29.3 min had ions of m/z (relative intensity): 181 (100%) and 460 (5%). In the CI spectra, an M + 1 ion of $m/z = 491$ was observed. A proposed reaction product assignment of pentane-2,4-dione was based on observed data.

Oxime at Retention Times 29.6 and 31.2 min

The oxime observed at retention times of 29.6 and 31.2 min had ions of m/z (relative intensity): 41 (18%), 108 (26%), 121 (26%), 124 (24%), 181 (75%), 194 (40%), 221 (60%), and 304 (100%). In the CI spectra, an M + 1 ion of $m/z = 404$ was observed. A proposed reaction product assignment of 1-(1-hydroxy-7,7-dimethyl-2,3,4,5,6,7-hexahydro-1*H*-inden-2-yl)ethanone was based on observed data.

PFBHA/BSTFA derivation of the oximes at 29.6 and 31.2 min showed a chromatographic peak shift in retention time to 30.9 min. Using acetonitrile for CI, an M + 1 ion of $m/z = 476$ was observed. These data were used to further verify the proposed assignment of the 29.6- and 31.2-min peaks.

Oxime at Retention Times 29.9 and 32.8 min

The oxime observed at retention times of 29.9 and 32.8 min had ions of m/z (relative intensity): 43 (15–20%), 109 (30%), 122 (20%), 138 (30%), 150 (25%), 181 (75%), 206 (100%), and 372 (45%). In the CI spectra, an M + 1 ion of $m/z = 404$ was observed. A proposed reaction product assignment of 1-(1-hydroxy-3*a*,7-dimethyl-2,3,3*a*,4,5,6-hexahydro-1*H*-inden-2-yl)ethanone was based on observed data.

PFBHA/BSTFA derivation of the oximes at 29.9 and 32.8 min showed a chromatographic peak shift in retention time to 29.1 min. Using acetonitrile for CI,

an M + 1 ion of $m/z = 476$ was observed. These data were used to further verify the proposed assignment of the 29.9- and 32.8-min peaks.

Oxime at Retention Time 31.5 min

The oxime observed at a retention time of 31.5 min had ions of m/z (relative intensity): 91 (20%), 172 (30%), 181 (45%), 204 (7.5%), 370 (100%), and 385 (35%). Using acetonitrile for CI, an M + 1 ion of $m/z = 386$ was observed. A proposed reaction product assignment of 3-oxo-1-(2,6,6-trimethylcyclohex-1-en-1-yl)butyl nitrate was based on observed data.

Oxime at Retention Times 31.9 and 33.3 min

The oxime observed at retention times of 31.9 and 33.3 min had ions of m/z (relative intensity): 91 (15%), 164 (20%), 181 (40%), 220 (100%), and 370 (7.5%). In the CI spectra, an M + 1 ion of $m/z = 418$ was observed. A proposed reaction product assignment of 3-oxo-1-(2,6,6-trimethylcyclohex-1-en-1-yl)butane-1,2-diyl dinitrate was based on observed data.

Oxime at Retention Times 35.5 min

The oxime observed at a retention time of 35.5 min had ions of m/z (relative intensity): 181 (100%), 304 (50%), 336 (90%), and 533 (6%). Using acetonitrile for CI, an M + 1 ion of $m/z = 531$ was observed. A proposed reaction product assignment of 3,3-dimetylcyclohexane-1,2-dione was based on observed data.

Oxime at Retention Times 39.6, 41.1, 41.5, and 43.1 min

The oxime observed at retention times of 39.6, 41.1, 41.5, and 43.1 min had ions of m/z (relative intensity): 181 (100%) and 488 (40%). No CI ions were observed. This was unexpected, since Arey et al. [29] observed this product using methane as the CI reagent, which gave the molecular ion of $m/z = 489$. A proposed reaction product assignment of 4-oxopent-2-enal was based on observed data.

Oxime at Retention Time 42.4 min

The oxime observed at a retention time of 42.4 min had ions of m/z (relative intensity): 181 (50%), 359 (100%), 360 (20%), and 375 (15%). Using acetonitrile for CI, an M + 1 ion of $m/z = 557$ was observed. A proposed reaction product assignment of (2*E*)-5-acetyl-2-ethylidene-3-methylcyclopentanone was based on observed data (Fig. 3).

DISCUSSION

The nitrate radical can react with β-ionone by H-atom abstraction or NO_3• addition to carbon-carbon double bonds [5,9,12,26]. Structure 1 shows the most likely sites for these nitrate radical reactions. The measured $k_{NO_3\cdot+\beta\text{-ionone}}$ of (9.4 ± 0.2) × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} and can be compared with the previously measured $k_{OH\cdot+\beta\text{-ionone}}$ of 118 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} [28] and its corresponding calculated value of 238 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, using AOPWIN estimation software [30]. Primary reactions are expected to occur at both double bonds of β-ionone; however, the measured rate constant (k_{OH}•) suggests that only one of the double bonds interacts with OH•. This observation of the reaction occurring at a single double bond may be comparable to the NO_3• reactions reported here by the formation of specific reaction products (e.g., 20.8 and 25.7 min), which likely occurs at the double bond (labeled A, Structure 1).

For the β-ionone + NO_3• reaction, the experimental parameters were set to minimize side reactions and highlight the NO_3• hydrogen abstraction and/or NO_3• addition. Furthermore, experiments were done with β-ionone + NO_2 (by-product of N_2O_5 thermal degradation) to determine whether any of the observed oxidation products were from these reactions. No reaction products were observed that appeared to be due to NO_2 chemistry. It is possible that NO_2 generated by the decomposition of the N_2O_5 may react with alkyl radicals, formed after reaction with NO_3•, leading to the formation of organic nitrates. However, no experiments were done to unravel these mechanisms. Also, no reaction products were observed with β-ionone + NO_3• in UHP N_2 environment, which suggests that O_2 must be present to form the oxidized products described in the following text. The possible mechanistic steps leading to product formation also are described in the following text.

Equivalent or Structurally Analogous Products Observed from β-ionone/OH• or β-ionone/O_3 Reactions

Several oxidation products were generated from β-ionone/NO_3• reactions that were similar to those previously observed from β-ionone/OH• or β-ionone/O_3 gas-phase reactions [28]. The mechanisms for the formation of these specific products were detailed by Forester et al. [28] and only a brief

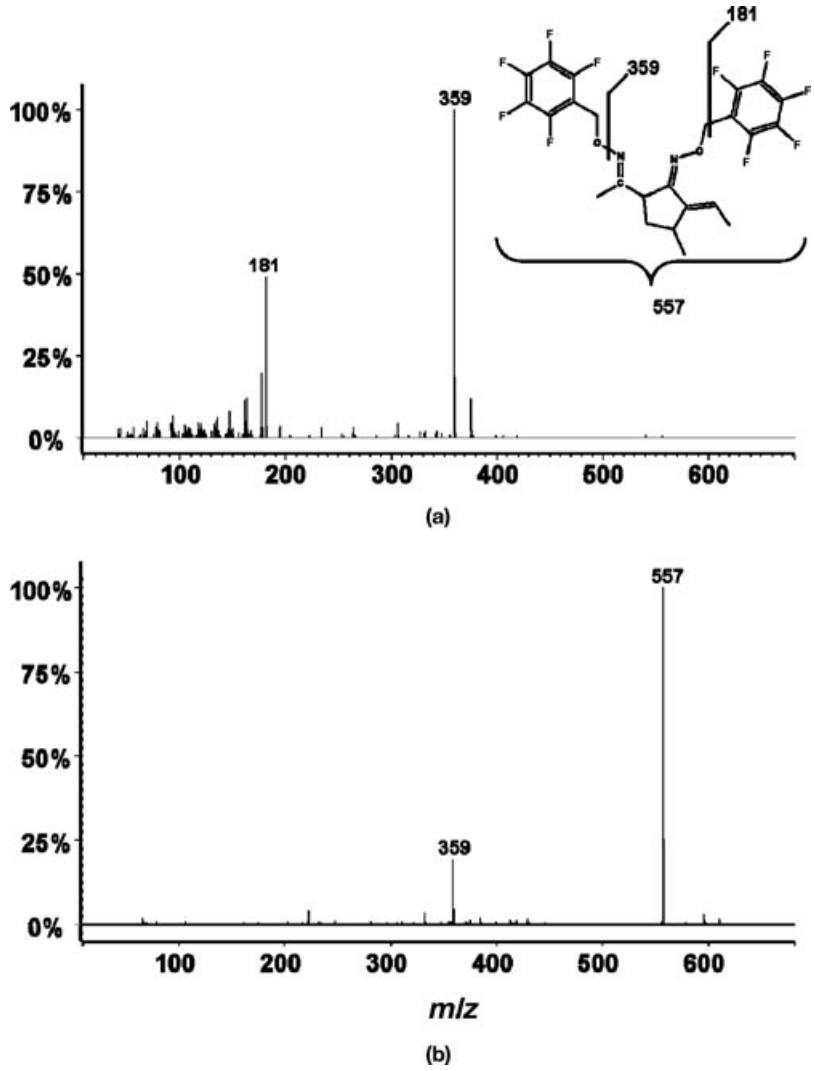


Figure 3 PFBHA-derivatized product of β-ionone + NO_3• (42.4 min): (a) electron ionization spectrum and (b) acetonitrile chemical ionization spectrum.

description will be provided here. The mechanism for the formation of the product observed at 20.8 min, (2*E*)-5-acetyl-2-ethylidene-3-methylcyclopentyl nitrate, is analogous to the similar product, 1-[(3*E*)-3-ethylidene-2-hydroxy-4-methylcyclopentyl]ethanone observed from β-ionone/OH•, except NO_3• adds to the carbon-carbon double bond (labeled A, Structure 1) with subsequent annelation of the alkyl radical leading to the five-membered ring. The proposed identity of this product was further supported by the observation of an ion at $m/z = 346$ using CI, which is due to the loss of one nitrate molecule ($m/z = 62$) and a hydrogen atom to give HNO_3. This loss has been commonly observed in mass spectra of alkyl and arylalkyl nitrates [31,32]. The product observed at 21.1 min (2,6,6-trimethylcyclohex-1-ene-1-carbaldehyde) was previously observed from reactions of β-ionone/OH• and β-ionone/O_3. The mechanism is similar to OH• and O_3 reactions by the interaction of NO_3• with the external carbon-carbon double bond leading to the formation of methylglyoxal and 2,6,6-trimethylcyclohex-1-ene-1-carbaldehyde (see mechanism illustrated in Fig. 4). The two oximes observed at 29.6 min (1-(1-hydroxy-7,7-dimethyl-2,3,4,5,6,7-hexahydro-1*H*-inden-2-yl)ethanone) and 29.9 min (1-(1-hydroxy-3*a*,7-dimethyl-2,3,3*a*,4,5,6-hexahydro-1*H*-inden-2-yl)ethanone) were also previously observed in β-ionone/OH• and β-ionone/O_3 gas-phase reactions. These two are products are formed by the initial addition of NO_3• to the external carbon-carbon double bond. NO_3• may be lost, leaving a radical that can subsequently react with O_2

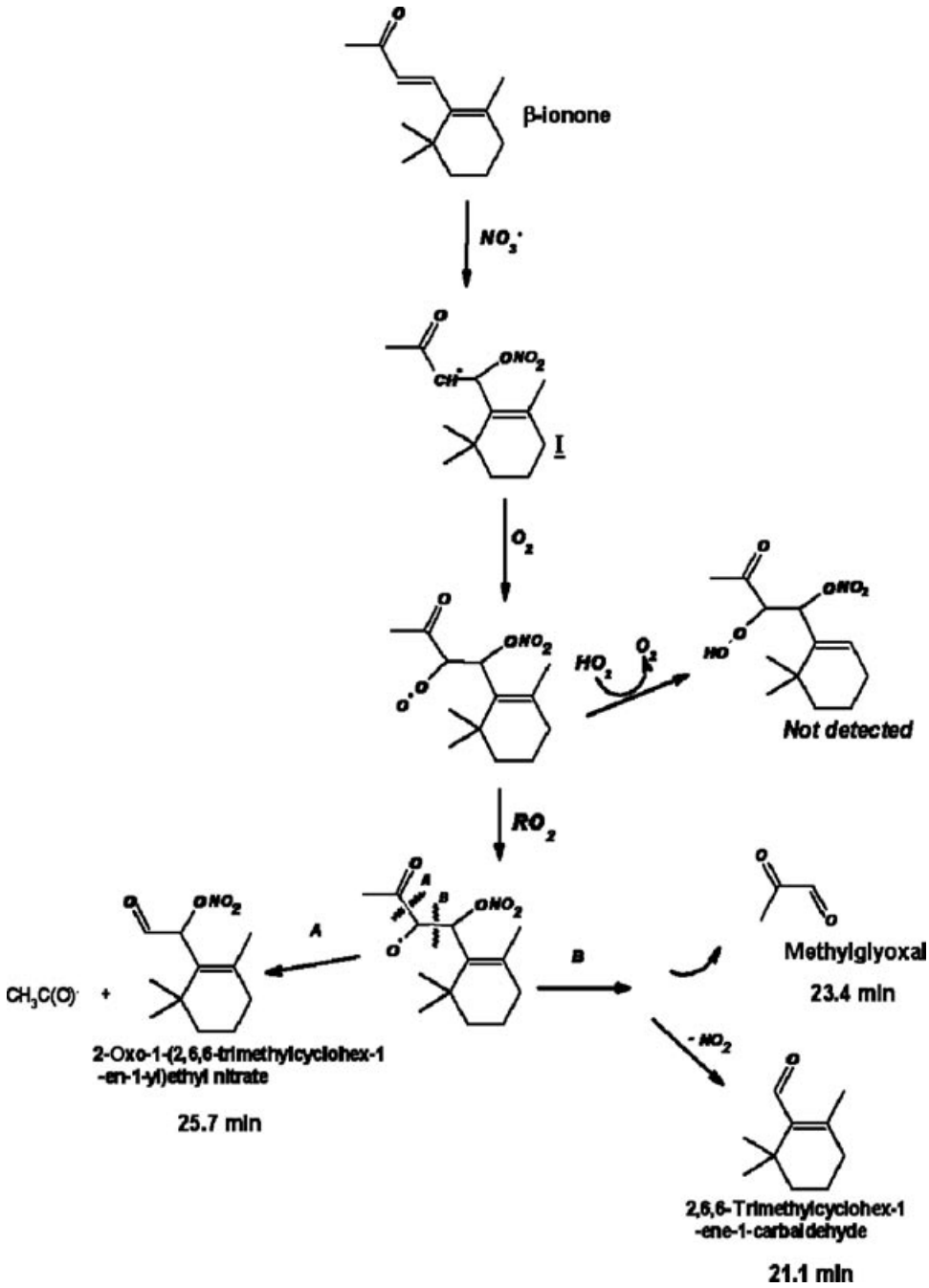


Figure 4 Proposed reaction mechanism for NO_3• addition to the external carbon-carbon double bond of β-ionone.

leading to the formation of a peroxy radical. Another peroxy radical (RO_2•) can react, resulting in the formation of an alcoholic OH as previously reported [33]. The adjacent radical can then undergo annelation leading to the ringed oxidation products. These types of cyclization are analogous to radical-mediated ring-closure mechanisms discussed in published literature [34–36]. Although the formation of the oximes (at 20.8, 29.6, and 29.9 min) generated by annelation in the gas phase seems energetically unfavorable, this may be overcome by an energy transfer via collisions of radicals in the gas phase or through stabilization in the impinger collection liquid.

The oxime product observed at 29.3 min (pentane-2,4-dione) is possibly formed by the addition of NO_3• to the internal carbon-carbon double bond (labeled B, Structure 1). The exact steps of this reaction product are unclear and proposal of a potential mechanism would

be difficult to suggest on the basis of conventional gas-phase VOC/NO_3• mechanisms. However, the proposed product assignment is reasonable given that this product is structurally similar to 4-oxopentanal, which has approximately the same retention time and same observed derivatized mass ($m/z = 491$). It was confirmed that the 29.3-min product was not wrongly identified as 4-oxopentanal by using a "pure" synthesized 4-oxopentanal standard, which was observed at 29.7, 30.1, and 30.4 min [37]. Only one peak was observed for pentane-2,4-dione; however, it is possible that the other derivatized isomers may be incorporated under this peak. Interestingly, the oxime observed at 29.3 min (pentane-2,4-dione) was not observed in previous β-ionone OH•/O_3 gas-phase experiments.

The oxime observed at 39.6 min ((2*E*)-4-oxopent-2-enal)) was also previously observed from β-ionone/OH• and β-ionone/O_3. This product is possibly formed by the addition of NO_3• to the internal carbon-carbon double bond (labeled B, Structure 1). This leads to the dissociation and formation of the carbonyl radical, $CH_3C(=O)CH=CHCH•$. The carbonyl radical can then react with O_2 to form the peroxy radical, $CH_3C(=O)CH=CHC(OO•)H$. This can further react with another RO_2 molecule to form $CH_3C(=O)CH=CHC(=O)H$. It is interesting that no CI ions (using acetonitrile as CI reagent) were observed for this product. Arey et al. [29] used PFBHA derivatization and were able to observe the molecular ion of $m/z = 489$ for this product using methane as the CI reagent.

Newly Observed β-ionone + NO_3• Reaction Products

The oxime at 25.7 min (2-oxo-1-(2,6,6-trimethylcyclohex-1-en-1yl)ethyl nitrate) (see Fig. 4) is formed by the reaction of NO_3• with the external carbon-carbon double bond of β-ionone leading to the formation of the carbon radical (**I**). This radical adds oxygen, forming the peroxy radical, which undergoes rearrangement with RO_2 and then dissociates following path A. The proposed identity of this product was made by the observation of an ion at $m/z = 360$ using CI, which can be due to the loss of one nitrate molecule ($m/z = 62$) and a hydrogen atom to make HNO_3 [31,32].

At present, the mechanistic pathways for the formation of the remaining proposed products that were observed in the gas-phase reaction of β-ionone + NO_3• are speculative. The exact steps of these reaction products maybe surface dependent and the proposal of a potential mechanism would be difficult to suggest on the basis of conventional gas-phase VOC/NO_3• mechanisms. However, the identities of these products may be inferred on the basis of fragmentation patterns and partial CI data. The proposed identity of the oxime at 11.4 min (3-oxobutane-1,2-diyl dinitrate) was made by the observation of an oxime ion at $m/z = 298$ using CI, which can be due to the loss of two NO_2 molecules ($m/z = 92$) [31,32]. 3,3-Dimethylcyclohexane-1,2-dione (35.5 min) is another proposed product and was suggested by the oxime molecular ion observed at $m/z = 531$. The proposed identity of the oxime at 31.5 min (3-oxo-1-(2,6,6-trimethylcyclohex-1-en-1-yl)butyl nitrate) was made by the observation of an ion at $m/z = 386$ using CI. The proposed identity of this product was based on the mass spectral fragmentation pattern and its expected reaction mechanism of NO_3• addition to the external carbon-carbon double bond. The β-ionone/dinitrate product, 3-oxo-1-(2,6,6-trimethylcyclohex-1-en-1-yl)butane-1,2-diyl dinitrate, (31.9 min) was proposed by the observation of an ion at $m/z = 418$ using CI, which is due to the loss of two NO_2 molecules ($m/z = 92$) [31,32].

It is possible that additional reaction products, such as hydroperoxides or nitrates without carbonyl groups, were formed but were not observed using the PFBHA and PFBHA/BSTFA derivatization techniques. In addition, oxidation products generated from these reactions may have been lost to the surface of the reaction chamber or inefficiency during impinger collection. In future experiments, the Teflon chamber may be rinsed to determine whether any oxidation products remain adsorbed to the chamber surface.

Indoor Nitrate Radical Chemistry

Indoor environment concentrations of the nitrate radical (2×10^7 molecules cm^{-3}) have been previously estimated by Sarwar et al. [38]. Using the β-ionone + NO_3• rate constant reported here, a pseudo-first-order rate constant (k') of 0.8 h^{-1} was determined. A comparison of this value to a typical indoor air exchange rate of 0.6 h^{-1} [39] suggests that nitrate radical chemistry is the most likely removal mechanism for β-ionone. When compared with the pseudo-first-order rate constants of the hydroxyl radical ($k_{OH•+β\text{-Ionone}} = 118 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, $k' = 0.05$ h^{-1}) and ozone ($k_{O_3+β\text{-ionone}} = 0.19 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1}, $k' = 0.03$ h^{-1}) [28], it is evident that nitrate radical chemistry could play a critical role in the transformation of β-ionone in the indoor environment.

Nitrate radical reactions can lead to a number of organic nitrate products such as PANs, alkyl nitrates, hydroxynitrates, and dinitrates [14]. Organic nitrates have received considerable interest because of their potential for deleterious health effects. However, only

minimal toxicity data exist for alkyl and arylalkyl nitrates, hydroxynitrates, and dinitrates. It is expected that these compounds may have harmful health effects and should be investigated. For example, nitro-PAHS (e.g., 6-nitrobenzo[*a*]pyrene, 3-nitroperylene, 1-nitropyrene, and 6-nitrochysene) formed from NO_3•/PAH reactions have been identified as mutagens and carcinogens [16]. Nevertheless, predictions of organic nitrate hazards can be made using the Hazassess program developed by Jarvis et al. [40,41]. Using this program, the calculated hazard index values of 2,6,6-trimethylcyclohex-1-ene-1-carbaldehyde and 3-oxo-1-(2,6,6-trimetylcyclohexane-1-en-1-yl)butane-1,2-diyl dinitrate were 0.66 and 0.57, respectively. Hazard index values of more than 0.5 are labeled as being "very probably hazardous" and are predicted to induce occupational asthma. Although this program should not be used to confirm the toxicity of these compounds, it does give insight into potential factors that can affect indoor air quality.

The findings and conclusions in this report are those of the author(s) and do not necessarily represent the official position of the Centers for Disease Control and Prevention/Agency for Toxic Substances and Disease Registry.

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