2-Butoxyethanol and Benzyl Alcohol Reactions with the Nitrate Radical: Rate Coefficients and Gas-Phase Products

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ABSTRACT: The bimolecular rate coefficients $k_{NO_3^\bullet+2\text{-butoxyethanol}}$ and $k_{NO_3^\bullet+\text{benzyl alcohol}}$ were measured using the relative rate technique at (297 ± 3) K and 1 atmosphere total pressure. Values of (2.7 ± 0.7) and (4.0 ± 1.0) $\times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} were observed for $k_{NO_3^\bullet+2\text{-butoxyethanol}}$ and $k_{NO_3^\bullet+\text{benzyl alcohol}}$, respectively. In addition, the products of 2-butoxyethanol + $NO_3^\bullet$ and benzyl alcohol + $NO_3^\bullet$ gas-phase reactions were investigated. Derivatizing agents O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine and N, O-bis (trimethylsilyl)trifluoroacetamide and gas chromatography mass spectrometry (GC/MS) were used to identify the reaction products. For 2-butoxyethanol + $NO_3^\bullet$ reaction: hydroxyacetaldehyde, 3-hydroxypropanal, 4-hydroxybutanal, butoxyacetaldehyde, and 4-(2-oxoethoxy)butan-2-yl nitrate were the derivatized products observed. For the benzyl alcohol + $NO_3^\bullet$ reaction: benzaldehyde ($(C_6H_5)C(=O)H$) was the only derivatized product observed. Negative chemical ionization was used to identify the following nitrate products: [(2-butoxyethoxy)(oxido)amino]oxidanide and benzyl nitrate, for 2-butoxyethanol + $NO_3^\bullet$ and benzyl alcohol + $NO_3^\bullet$, respectively. The elucidation of these products was facilitated by mass spectrometry of the derivatized reaction products coupled with a plausible 2-butoxyethanol or benzyl alcohol + $NO_3^\bullet$ reaction mechanisms based on previously published volatile organic compound + $NO_3^\bullet$ gas-phase mechanisms. © 2012 Wiley Periodicals, Inc.* Int J Chem Kinet 1–11, 2012

INTRODUCTION

Indoor environment concentrations of the nitrate radical ($NO_3^\bullet$), an important reactive species, have been estimated by Sarwar et al. to be approximately 1.1 parts per trillion (ppt) (2×10^7 molecules/cm^3) [1]. The indoor concentrations of volatile organic compounds (VOCs) can be elevated from activities such as cleaning, washing, and painting and as a result of building energy-saving measures [2,3]. Therefore, in the indoor environment, reactions between VOCs and $NO_3^\bullet$ are possible and based on previous VOC/$NO_3^\bullet$ rate

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coefficient measurements, the transformation of VOCs into oxygenated organic reaction products can effectively compete with building air exchange [4]. Potential VOC oxidation products include alcohols, aldehydes, ketones, dicarbonyls, carboxylic acids, and organic nitrates [5–7]. These products have the potential to cause a number of adverse health effects including asthma, allergy, and respiratory irritation [8,9].

Benzyl alcohol, an aromatic primary alcohol, is used as a solvent in paint stripper and waterborne-coating applications and as an intermediate for the synthesis of target molecules used in pharmaceuticals, cosmetics, preservatives, and flavoring and fragrance agents. Production capacity worldwide of benzyl alcohol is estimated at 50 kT [10]. The $k_{\mathrm{OH}^\bullet+\text{benzyl alcohol}}$ ($(28 \pm 7) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}) and the $k_{\mathrm{O3}+\text{benzyl alcohol,}}$ ($\sim 6 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1}) and the respective reaction products have been investigated previously [11]. Liu et al. have investigated electric plugin air freshener emissions and found the benzyl alcohol concentration reached a maximum of about 0.05 ppm (1.2×10^{12} molecule cm^{-3}) after about 50 h and remained relatively stable even after ozone was introduced into the system [12].

2-Butoxyethanol, a butyl ether of ethylene glycol, is used as a solvent in paints and surface coatings and other consumer products such as inks, cleaning products, liquid soaps, and oil spill dispersants. Worldwide production of 2-butoxyethanol in 1994 was estimated to be 300 kT [13]. The $k_{\mathrm{OH}^\bullet+\text{2-butoxyethanol}}$ (18.6×10^{-12} cm^3 molecule^{-1} s^{-1}) [14] and the reaction products have been investigated [15]. A recent assessment of emissions from a typical consumer glass cleaner showed concentrations of 0.04–0.17 ppm (1.0–4.2×10^{12} molecule cm^{-3}) of 2-butoxyethanol for about 4 h after cleaning [16]. Other studies have suggested that 2-butoxyethanol emissions will continue over hours or even days after using a product containing this chemical [17,18]. Exposures may take place both during the cleaning process and from remnants left after cleaning.

In this study, the kinetics and reaction products of benzyl alcohol and 2-butoxyethanol with $\mathrm{NO}_3^\bullet$ have been determined. This is important for assessing occupant exposures since both chemicals are in wide use, and the products formed could be potential human health hazards. The relative rate technique was used to determine the $\mathrm{NO}_3^\bullet$ reaction kinetics of benzyl alcohol and 2-butoxyethanol using gas chromatography/mass spectrometry (GC/MS). Products from the reaction of these chemicals and $\mathrm{NO}_3^\bullet$ were determined using the chemical derivatization agents *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) and *N*, *O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) with GC/MS and also using negative chemical ionization (NCI) mass spectrometry to detect gas-phase nitrate species.

EXPERIMENTAL

Apparatus and Materials

Experiments to measure the gas-phase rate coefficient of the $\mathrm{NO}_3^\bullet$ + 2-butoxyethanol and benzyl alcohol reactions were conducted with a previously described apparatus [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 $\mathrm{CaSO_4}$ (Drierite, Xenia, OH) and molecular sieves (Drierite) 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, Andover, MA). Analysis of this treated compressed air by gas chromatography/mass spectrometry revealed that if contaminants were present they would be below the part per trillion range. The treated compressed air was also analyzed for nitric oxide (NO) using a Thermo Electron model 42i NO–$\mathrm{NO_2}$–NO_x analyzer (Waltham, MA) and showed that 6 ppb (1.4×10^{11} molecule cm^{-3}) NO is present in the background in NIOSH air. 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 air stream. All reactant mixtures and calibration standards were generated by this system. An additional port was added to the Teflon chamber to facilitate the injection of $\mathrm{N_2O_5}$ (synthesis described below).

Two separate 65-L Teflon-film reaction chambers were used in these experiments. The reaction chamber contents were sampled for 5 min, using a solid-phase micro-extraction (SPME) fiber (Supelco, Milwaukee, WI), which was then inserted through a Merlin Microseal (Half Moon Bay, CA) and into the heated injector of either one of two (Agilent, Wilmington, DE) 6890 gas chromatographs each with a 5975 mass selective detector (GC/MS) and Agilent ChemStation software. The GC temperature program used was the same for both systems: An injection port was set to 250°C, and the oven temperature began at 40°C for 6 min and was ramped 20°C min^{-1} to 240°C and held for 2 min. All data were compiled from both systems and were used to determine the $\mathrm{NO}_3^\bullet$ rate coefficient for each of the compounds

Identification of reaction products was made using PFBHA to derivatize carbonyl products, whereas carbonyl alcohols were derivatized using BSTFA [20]. Experimental methods for reaction product identification were similar to methods used for kinetic experiments, except the reference compound was excluded from the reaction mixture.

Derivatized reaction products were analyzed using a Varian (Palo Alto, CA) 3800/Saturn 2000 GC/MS system operated in both the electron ionization (EI) and chemical ionization (CI) modes [20]. Compound separation was achieved by a J&W Scientific (Folsom, CA) DB-5MS (0.32 mm i.d., 30-m long, 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 perfluorotributylamine (FC-43). Full-scan EI spectra were collected from m/z 40 to 650. Acetonitrile was the 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 products were analyzed using NCI on an Agilent (Wilmington, DE) 6890 gas chromatograph with a 5975 mass selective detector (GC/MS) and Agilent ChemStation software. The GC temperature program used was the injection port was set to 150°C and oven temperature began at 30°C for 2 min and was ramped 8°C min^{-1} to 150°C and held for 16 min and then ramped 20°C min^{-1} to 220°C and held for 5 min. Full-scan NCI spectra were collected from m/z 40 to 700. Hydrogen was the CI reagent used for all NCI spectra.

Nitrate radicals were generated by the thermal decomposition of N_2O_5 using a similar method as described by Atkinson et al. [5,21]. N_2O_5 (solid) kept at –85°C was removed from cold trap and allowed warm slightly and transferred to an evacuated 2-L collection bottle until manifold pressure was between 0.1–0.6 Torr. The collection bottle was then pressurized with ultra-high purity 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 30 min elapsed before any samples were collected after the introduction of N_2O_5. Initial experiments with just the individual reference, N_2O_5, and compound of interest are run prior to combining all of these to ensure that the compounds or products do not have retention times that interfere with peaks that are used for the relative rate technique.

All compounds were used as received and had the following purities: from Sigma-Aldrich (Milwaukee, WI): benzaldehyde (99%), 1,3,5-trimethylbenzene (mesitylene) (98%), 4-isopropyltoluene (p-cymene) (99%), 2-butoxyethanol (99.5%), benzyl alcohol (99.8%), acetonitrile (99.93%), BSTFA (99%), O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) (98+%), and methanol (99%). Nitrogen dioxide as a 5% mixture in nitrogen and ultra-high purity (UHP) oxygen was 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 1 atmosphere pressure.

Procedures

The experimental procedures for determining the 2-butoxyethanol or benzyl alcohol (alcohols) + $NO_3^\bullet$ reaction kinetics were similar to those described previously [19]. The $NO_3^\bullet$ rate coefficient experiments for 2-butoxyethanol employed the use of two reference compounds: benzaldehyde and mesitylene. The $NO_3^\bullet$ rate coefficient experiments for benzyl alcohol employed the use of two reference compounds: p-cymene and mesitylene:

$$\text{Alcohols} + \text{NO}_3^\bullet \xrightarrow{k_{\text{NO}_3+\text{Alcohols}}} \text{Products} \tag{1}$$

$$\text{Reference} + \text{NO}_3^\bullet \xrightarrow{k_{\text{Ref}}} \text{Products} \tag{2}$$

The rate equations for reactions (2) and (3) are combined and integrated, resulting in the following equation:

$$\ln\left(\frac{[\text{Alcohols}]_0}{[\text{Alcohols}]_t}\right) = \frac{k_{\text{NO}_3+\text{Alcohols}}}{k_{\text{Ref}}} \ln\left(\frac{[\text{Ref}]_0}{[\text{Ref}]_t}\right) \tag{3}$$

If a reaction with $NO_3^\bullet$ is the only removal mechanism for 2-butoxyethanol or benzyl alcohol (Alcohols) and reference, a plot of $\ln([\text{Alcohols}]_0/[\text{Alcohols}]_t)$ versus $\ln([\text{Ref}]_0/[\text{Ref}]_t)$ yields a straight line with an intercept of zero. Multiplying the slope of this linear plot by k_{Ref} yields $k_{\text{NO}_3^\bullet+\text{2-butoxyethanol}}$ or $k_{\text{NO}_3^\bullet+\text{benzyl alcohol}}$ (Figs. 1 and 2). Using two different reference compounds with different $NO_3^\bullet$ rate coefficients improves the accuracy of the 2-butoxyethanol/$NO_3^\bullet$ or benzyl alcohol/$NO_3^\bullet$ rate coefficient measurement. The simultaneous plotting of two Alcohols/Ref data sets

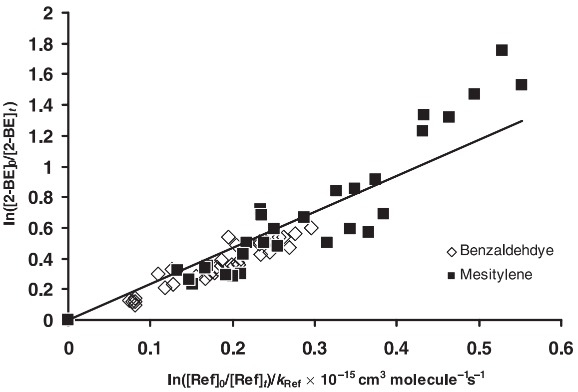


Figure 1 2-Butoxyethanol relative rate plot with benzaldehyde (◇) and mesitylene (■) as reference compounds. The $NO_3^\bullet$ + 2-butoxyethanol rate coefficient, $k_{NO_3^\bullet+\text{2-butoxyethanol}}$, was measured to be (2.7 ± 0.7) × 10^{-15} cm^3 molecule^{-1} s^{-1}.

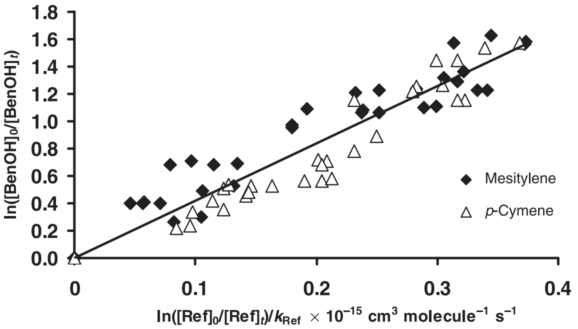


Figure 2 Benzyl alcohol relative rate plot with p-cymene (△) and mesitylene (◆) as reference compounds. The $NO_3^\bullet$ + benzyl alcohol rate coefficient, $k_{NO3^\bullet+\text{benzyl alcohol}}$, was measured to be (4.0 ± 1.0) × 10^{-15} cm^3 molecule^{-1} s^{-1}.

demonstrates that other reactions are not removing 2-butoxyethanol or benzyl alcohol.

For the 2-butoxyethanol/$NO_3^\bullet$ and benzyl alcohol/$NO_3^\bullet$ kinetic experiments, the typical concentrations of the pertinent species in the 65-L Teflon chamber were 0.3–0.9 ppm ((0.7–2) × 10^{13} molecule cm^{-3}) 2-butoxyethanol or benzyl alcohol, 0.3–0.8 ppm ((0.7–2.0) × 10^{13} molecule cm^{-3}) reference, 3.9–23 ppm ((1–5.7) × 10^{14} molecule cm^{-3}) of N_2O_5 (0.1–0.6 Torr, which corresponds to an $NO_3^\bullet$ concentration of 0.3–1.5 ppm at 298 K) 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) peak area from the Agilent 5973 mass selective detector was used to determine 2-butoxyethanol/benzyl alcohol 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 methanol with no effort to prevent methanol evaporation during sample collection. The sample was removed from the impinger, and 100 μL was withdrawn and analyzed using NCI. To the remaining sample solution (approximately 2 mL), 250 μL of 0.02 M PFBHA in acetonitrile was added to derivatize the carbonyl reaction products to oximes [20]. This solution was allowed to react for 24–48 h 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 with 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 [22].

RESULTS

2-Butoxyethanol/$NO_3^\bullet$ Reaction Rate Coefficient

The $NO_3^\bullet$ rate coefficient for 2-butoxyethanol 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 coefficient (benzaldehyde (2.4 ± 0.5) × 10^{-15} cm^3 molecule^{-1} s^{-1} or mesitylene (8.8 ± 2.2) × 10^{-16} cm^3 molecule^{-1} s^{-1}) [23] and multiplied by 10^{-15} cm^3 molecule^{-1} s^{-1}, resulting in a unitless number. This yields a slope that is equal to the $NO_3^\bullet$/2-butoxyethanol rate coefficient, $k_{NO_3^\bullet+\text{2-butoxyethanol}}$, divided by 10^{-15} cm^3 molecule^{-1} s^{-1}. This modification allows for a simultaneous comparison of the two reference compound/2-butoxyethanol data sets. The slope of the line shown in Fig. 1 yields an $NO_3^\bullet$ bimolecular rate coefficient, $k_{NO_3^\bullet+\text{2-butoxyethanol}}$, of (2.7 ± 0.2) × 10^{-15} cm^3 molecule^{-1} s^{-1}. The use of benzaldehyde and mesitylene as references resulted in $NO_3^\bullet$ + 2-butoxyethanol bimolecular rate coefficients of (2.0 ± 0.2) and (2.9 ± 0.4) × 10^{-15} cm^3 molecule^{-1} s^{-1}, respectively (see Table I). The data points at the origin are experimental points before $NO_3^\bullet$ addition, $t = 0$, data showed no detectable loss of 2-butoxyethanol or reference. The error in the rate coefficient stated above is the 95% confidence level from the random uncertainty in the slope. Incorporating the uncertainties associated with the reference rate

Table I Rate Constants Measured from 2-Buoxyethanol/Benzyl Alcohol + $NO_3^\bullet$ Reaction

Compound	Reference	k_{alc}/k_{ref}	k_{alc}[cm^3 molecule^{-1} s^{-1}]
2-Butoxyethanol	Benzaldehdye	1.0	2.0×10^{-15}
2-Butoxyethanol	Mesitylene	3.1	2.9×10^{-15}
2-Butoxyethanol	Overall		2.7×10^{-15}
Benzyl alcohol	*p*-Cymene	4.0	4.3×10^{-15}
Benzyl alcohol	Mesitylene	5.0	4.0×10^{-15}
Benzyl alcohol	Overall		4.0×10^{-15}

coefficients (±25% for benzaldehyde and mesitylene) [23] used to derive the 2-butoxyethanol/$NO_3^\bullet$ rate coefficient yields a final value for $k_{NO_3^\bullet+2\text{-butoxyethanol}}$, of (2.7 ± 0.7) × 10^{-15} cm^3 molecule^{-1} s^{-1} [23]. The ratios $k_{NO_3^\bullet+2\text{-butoxyethanol}}/k_{NO_3^\bullet+\text{benzaldehyde}}$ and $k_{NO_3^\bullet+2\text{-butoxyethanol}}/k_{NO_3^\bullet+\text{mesitylene}}$ incorporating the uncertainties are 1.0 ± 0.3 and 3.1 ± 0.8, respectively. The 2-butoxyethanol/$NO_3^\bullet$ rate coefficient, $k_{NO_3^\bullet+2\text{-butoxyethanol}}$, has not been previously reported.

Benzyl Alcohol/$NO_3^\bullet$ Reaction Rate Coefficient

The $NO_3^\bullet$ rate coefficient for benzyl alcohol was also obtained using the relative rate method, and a plot of a modified version of Eq. (3) is shown in Fig. 2. The $\ln([\text{Ref}]_0/[\text{Ref}]_t)$ term is divided by the respective reference rate coefficient (*p*-cymene (1.0 ± 0.3) × 10^{-15} cm^3 molecule^{-1} s^{-1} and mesitylene (8.8 ± 2.2) × 10^{-16} cm^3 molecule^{-1} s^{-1}) [23] and multiplied by 10^{-15} cm^3 molecule^{-1} s^{-1}. The slope of the line shown in Fig. 2 yields an $NO_3^\bullet$ bimolecular rate coefficient, $k_{NO_3^\bullet+\text{benzyl alcohol}}$, of (4.1 ± 0.3) × 10^{-15} cm^3 molecule^{-1} s^{-1}. The use of *p*-cymene and mesitylene as references resulted in $NO_3^\bullet$ + benzyl alcohol bimolecular rate coefficients of (4.3 ± 0.4) and (4.0 ± 0.4) × 10^{-15} cm^3 molecule^{-1} s^{-1}, respectively (see Table I). The error in the rate coefficient stated above is the 95% confidence level from the random uncertainty in the slope. Incorporating the uncertainties associated with the reference rate coefficients (±25% for *p*-cymene and mesitylene) [23] used to derive the benzyl alcohol/$NO_3^\bullet$ rate coefficient yields a final value for $k_{NO_3^\bullet+\text{benzyl alcohol}}$, of (4.0 ± 1.0) × 10^{-15} cm^3 molecule^{-1} s^{-1}. The ratios $k_{NO_3^\bullet+\text{benzyl alcohol}}/k_{NO_3^\bullet+p\text{-cymene}}$ and $k_{NO_3^\bullet+\text{benzyl alcohol}}/k_{NO_3^\bullet+\text{mesitylene}}$ incorporating the uncertainties are 4.0 ± 1.0 and 5.0 ± 1.0, respectively. The benzyl alcohol/$NO_3^\bullet$ rate coefficient, $k_{NO_3^\bullet+\text{benzyl alcohol}}$, has not been previously reported.

2-Butoxyethanol/$NO_3^\bullet$ and Benzyl Alcohol/$NO_3^\bullet$ Reaction Products Using PFBHA and NCI

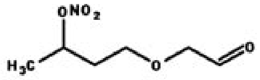
Derivatization of nonsymmetric carbonyls using PFBHA or PFBHA/BSTFA typically resulted in multiple chromatographic peaks due to stereoisomers of the oximes. Identification of multiple peaks of the same oxime compound is relatively simple since the mass spectra for each chromatographic peak of a particular oxime are almost identical [20]. In most cases, the *m*/*z* 181 ion relative intensity for the chromatographic peaks due to 2-butoxyethanol + $NO_3^\bullet$ or benzyl alcohol + $NO_3^\bullet$ reaction product oximes was the base peak in the mass spectrum and was used to generate selected ion chromatograms. The mass spectra of compounds additionally derivatized with BSTFA could contain *m*/*z* 73 ion from the $[Si(CH_3)_3]^+$ fragments [20]. The product data are described below.

The following chromatographic retention time and mass spectra data were observed utilizing PFBHA derivatization and the Varian 3800/Saturn 2000 GC/MS system. The reaction products' chromatographic peak areas were a function of the initial 2-butoxyethanol/benzyl alcohol concentration and were observed only after $NO_3^\bullet$ initiation of 2-butoxyethanol/benzyl alcohol/methanol/air mixtures. Derivatization experiments performed in the absence of 2-butoxyethanol or benzyl alcohol, but in the presence of all other chemicals in the reaction chamber ($NO_3^\bullet$/air/methanol) did not result in any of the data reported below.

The PFBHA reaction products observed from the 2-butoxyethanol/$NO_3^\bullet$ via hydrogen abstraction are hydroxyacetaldehyde, 3-hydroxypropanal, 4-hydroxybutanal, and butoxyacetaldehyde and 4-(2-oxoethoxy)butan-2-yl nitrate. The PFBHA reaction product observed from the benzyl alcohol/$NO_3^\bullet$ via hydrogen abstraction was benzaldehyde. Elucidation of the proposed reaction products for 2-butoxyethanol (listed in Table II) was facilitated by mass spectrometry of the derivatized reaction product coupled with plausible 2-butoxyethanol/$NO_3^\bullet$ reaction mechanisms based on the previously published VOC/$NO_3^\bullet$ gas-phase reaction as described below [7,23–27].

The chromatographic retention time and mass spectra data were observed for NCI utilizing the Agilent 6890/5975 GC/MS system. TIC from the Agilent 5973 mass selective detector was used to determine products for 2-butoxyethanol/$NO_3^\bullet$ and benzyl alcohol/$NO_3^\bullet$ reactions. The reaction products' chromatographic peak areas were a function of the initial 2-butoxyethanol/benzyl alcohol concentration and were observed only after $NO_3^\bullet$ initiation

Table II Products Observed from 2-Buoxyethanol + $NO_3^\bullet$ Reaction

Retention Time (min)	Structure	Molecular Weight (amu)	CI Ions Observed
10.0 10.3	 2-Hydroxyacetaldehyde	60	256
10.0 10.3 10.5	 3-Hydroxypropanal	74	270
10.5	 4-Hyrdroxybutanal	88	284
13.8	 Butoxyacetaldehyde	116	312
16.1	 4-(2-Oxoethoxy)butan-2-yl nitrate	177	326
Negative chemical ionization spectra			
18.5	 [(2-Butoxyethoxy)(oxido)amino]oxidanide	163	163

of 2-butoxyethanol/benzyl alcohol/methanol/air mixtures. Experiments performed in the absence of 2-butoxyethanol or benzyl alcohol, but in the presence of all other chemicals in the reaction chamber ($NO_3^\bullet$/air/methanol) did not result in any of the data reported below. The presence of a strong *m*/*z* 46 ion relative intensity is an indicator of a nitrate product [28,29].

Oxime at Retention Time of 10.0 and 10.3 min

The oxime observed with a chromatographic retention time of 10.0 and 10.3 min had ions of *m*/*z* (relative intensity): 57 (8%), 99 (8%), 117 (8%), 161 (8%), 181 (100%), 195 (19%), 226 (6%), and 238 (5%). In the CI spectra, an M + 1 ion of *m*/*z* 256 was observed for the PFBHA-derivatized sample. The *m*/*z* 256 ion is the result of a PFBHA derivatization, indicating a reaction product with a molecular weight of 60. A proposed reaction product assignment of hydroxyacetaldehyde ($CH(=O)CH_2OH$) (glycolaldehyde) was based on the observed data and previous investigations [22].

Oxime at Retention Time of 10.0, 10.3, and 10.5 min

The oxime observed with a chromatographic retention time of 10.0, 10.3, and 10.5 min had ions of *m*/*z* (relative intensity): 99 (7%), 117 (7%), 161 (6%), 181 (100%), 194 (18%), 225 (17%), and 238 (7%). In the CI spectra, an M + 1 ion of *m*/*z* 270 was observed for the PFBHA-derivatized sample. The *m*/*z* 270 ion is the result of a PFBHA derivatization, indicating a reaction product with a molecular weight of 74. A proposed reaction product assignment of 3-hydroxypropanal ($CH(=O)CH_2CH_2OH$) was based on the observed data.

Oxime at Retention Time of 10.5 min

The oxime observed with a chromatographic retention time of 10.5 min had ions of *m*/*z* (relative intensity): 99 (7%), 117 (7%), 161 (7%), 181 (100%), 195 (11%), and 238 (8%). In the CI spectra, an M + 1 ion of *m*/*z* 284 was observed for the PFBHA-derivatized sample. The *m*/*z* 284 ion is the result of a PFBHA derivatization, indicating a reaction product with a molecular weight of 88. A proposed reaction product assignment of

4-hydroxybutanal ($CH(=O)CH_2CH_2CH_2OH$) was based on the observed data.

Oxime at Retention Time of 13.6 min

The oxime observed with a chromatographic retention time of 13.6 min had ions of m/z (relative intensity): 57 (16%), 99 (7%), 161 (8%), 181 (100%), 195 (8%), 207 (12%), 225 (14%), and 239 (17%). In the CI spectra, an M + 1 ion of m/z 312 was observed for the PFBHA-derivatized sample. The m/z 312 ion is the result of a PFBHA derivatization, indicating a reaction product with a molecular weight of 116. A proposed reaction product assignment of butoxyacetaldehyde ($CH_3CH_2CH_2CH_2OCH_2CH(=O)$) was based on the observed data.

Oxime at Retention Time of 16.1 min

The oxime observed with a chromatographic retention time of 16.1 min had ions of m/z (relative intensity): 45 (6%), 57 (15%), 71 (17%), 99 (6%), 117 (6%), 161 (7%), 181 (100%), 195 (9%), and 255 (16%).%). In the CI spectra, an M + 1 ion of m/z 326 was observed for the PFBHA-derivatized sample. The m/z 326 ion is the result of a PFBHA derivatization, indicating a reaction product with a molecular weight of 177. The major ion observed at 16.1 min was $m/z = 131$, which is probably due to the loss of one NO_2 molecule ($m/z = 46$). A proposed reaction product assignment of 4-(2-oxoethoxy)butan-2-yl nitrate ($CH_3CH(NO_2)CH_2CH_2OCH_2CH(=O)$) was based on the observed data.

PFBHA and BSTFA can be utilized in a two-step derivatization method (see above) to derivatize compounds that contain both a carbonyl and a hydroxyl group. The oximes at retention times of 10.0, 10.3, and 10.5 min are proposed products, all of which contain a carbonyl and hydroxyl group. PFBHA/BSTFA experiments were attempted but were unsuccessful in capturing any of the oximes with the hydroxyl group at retention times 10.0, 10.3, and 10.5 min. The lack of observation could be due to their low product yield coupled with inefficient derivatization chemistry. No evidence of any fragments was observed at m/z 73 ions, which is a characteristic ion of the OH functional group derivatization [20]. Glycolaldehyde has been observed by this group, and both the mass spectrum and retention times are in good agreement with previous work [22].

NCI 2-Butoxyethanol Nitrate Product at 18.5 min

For 2-butoxyethanol, the ion at a chromatographic retention time of 18.5 min had ions of m/z (relative intensity) 46 (100%), 58 (18%), 90 (22%), 115 (70%), and 117 (25%). The proposed identity of the ion at 18.5 min was made by observance of an ion at $m/z = 117$, which is due to the loss of one NO_2 molecule ($m/z = 46$). This loss has been commonly observed in mass spectra of alkyl and arylalkyl nitrates [28,29]. The m/z 117 ion observed in the NCI spectrum indicates a reaction product with a molecular weight of 163. A proposed reaction product assignment of [(2-butoxyethoxy)(oxido) amino]oxidanide ($CH_3CH_2CH_2CH_2OCH_2CH_2ONO_2$) was based on the observed data.

The PFBHA reaction product observed from the benzyl alcohol/$NO_3^\bullet$ via hydrogen abstraction is benzaldehyde. The benzyl alcohol/$NO_3^\bullet$ reaction product observed and positively identified using the pure compound for verification by derivatization was benzaldehyde.

Benzaldehyde ($(C_6H_5)C(O)H$)

The oxime observed with a chromatographic retention time of 17.2 and 17.5 min had ions of m/z (relative intensity) 181 (100%), 271 (38%), 300 (27%), 301 (55%), and 302 (11%). The m/z 301 ion is the result of a PFBHA derivatization, indicating a reaction product with a molecular weight of 106. Using acetonitrile for CI, an M + 1 ion of m/z of 302 was observed for the PFBHA-derivatized sample. The PFBHA-benzaldehyde oxime was synthesized to confirm this chromatographic assignment [11].

NCI Benzyl Alcohol Nitrate Product at 21.1 min

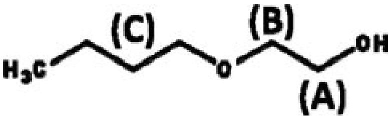
For benzyl alcohol, the ion at a chromatographic retention time of 21.1 min had ions of m/z (relative intensity) 46 (90%), 62 (10%), 77 (38%), 105 (100%), and 107 (60%). The proposed identity of the ion at 21.1 min was made by observance of an ion at $m/z = 107$, which is due to the loss of one NO_2 molecule ($m/z = 46$). The m/z 107 ion observed in the NCI spectrum indicates a reaction product with a molecular weight of 153. A proposed reaction product assignment of benzyl nitrate ($(C_6H_5)CH_2ONO_2$) was based on the observed data.

DISCUSSION

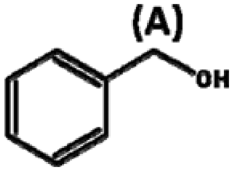
A rate coefficient of (2.7 ± 0.7) × 10^{-15} cm^3 $molecule^{-1}$ s^{-1} was determined for the reaction of $NO_3^\bullet$ and 2-butoxyethanol using benzaldehyde and mesitylene as references (Fig. 1). Even though the same number of data points was collected for each 2-butoxyethanol reference pair, the kinetic plot shows a wider distribution of data points for the 2-butoxyethanol/mesitylene pair. This wider distribution is likely due to mesitylene's $NO_3^\bullet$ rate coefficient being a factor of 3 slower than benzaldehyde's $NO_3^\bullet$ rate coefficient. It should be noted that the individual 2-butoxyethanol/$NO_3^\bullet$ rate coefficients determined using a single reference were (2.0 ± 0.2) × 10^{-15} cm^3 $molecule^{-1}$ s^{-1} and (2.9 ± 0.4) × 10^{-15} cm^3 $molecule^{-1}$ s^{-1} for benzaldehyde and mesitylene, respectively. It can be observed that these two rate coefficients are not within the 95% confidence limit regression error of each other as has been typically observed by this group. However, the discrepancy in the references' rate coefficients does not significantly impact the determined 2-butoxyethanol $NO_3^\bullet$ rate coefficient from the entire data set.

Rate Coefficient Data Comparison Ratio

The nitrate radical ($NO_3^\bullet$) like the hydroxyl radical ($OH^\bullet$) can react with VOC by H-atom abstraction and/or addition to carbon–carbon double bonds [7,25,27,30]. (Structures 1 and 2 show the sites for these nitrate radical reactions.) The similarity of these reactants' mechanisms could be used to address the limited number of measured $NO_3^\bullet$ rate coefficients by comparing measured $OH^\bullet$ rate coefficients and $NO_3^\bullet$ rate coefficients. Using the value determined here, the measured $k_{NO_3^\bullet+2\text{-butoxyethanol}}$ of (2.7 ± 0.7) × 10^{-15} cm^3 $molecule^{-1}$ s^{-1} and the previously measured $k_{OH^\bullet+2\text{-butoxyethanol}}$ of 18.6 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} [14] can be compared to one another. The ratio of rate coefficients ($k_{OH^\bullet}/k_{NO_3^\bullet}$) is 6889 for 2-butoxyethanol. Likewise for benzyl alcohol, the ratio of rate coefficients ($k_{OH^\bullet}/k_{NO_3^\bullet}$) is 7000 [11]. The similarity of these two ratios prompts an expanded comparison.



Structure 1. 2-Butoxyethanol.



Structure 2. Benzyl alcohol.

An overall ratio of rate coefficients $k_{OH^\bullet}/k_{NO_3^\bullet}$ can be estimated by using the average alcohol rate coefficient values for $k_{OH^\bullet}$ and $k_{NO_3^\bullet}$. These average values can be determined from published measurements from Atkinson and Arey for all of the alcohols rate coefficients that have been measured [23]. To date, the average alcohol $k_{OH^\bullet}$ is 9.7 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} and the average alcohol $k_{NO_3^\bullet}$ is 1.4 × 10^{-15} cm^3 $molecule^{-1}$ s^{-1} (20 alcohol $k_{OH^\bullet}$ measurements and 4 alcohol $k_{NO_3^\bullet}$ measurements) [23]. Using these average values, the ratio of rate coefficients $k_{OH^\bullet}/k_{NO_3^\bullet}$ for the entire set of alcohols that have been measured to date is 6929, which is consistent with the rate coefficient ratio from the measurements presented here. Dividing known $k_{OH^\bullet}$ alcohol rate coefficients by 7000 may be a suitable approach for approximating unknown $k_{NO_3^\bullet}$ alcohol rate coefficients.

2-Butoxyethanol/ $NO_3^\bullet$ PFBHA Reaction Products

For the 2-butoxyethanol + $NO_3^\bullet$ and benzyl alcohol + $NO_3^\bullet$ reactions, the experimental parameters were set to minimize side reactions and highlight the $NO_3^\bullet$ hydrogen abstraction and/or $NO_3^\bullet$ addition. The possible mechanistic steps leading to product formation are described below. The NO_2 is present due to the dissociation of N_2O_5 into $NO_3^\bullet$ and NO_2.

Oximes at Retention Time of 10.0, 10.3, and 10.5 min. The oximes proposed as 2-hydroxyacetaldehyde ($CH(=O)CH_2OH$) (glycolaldehyde), 3-hydroxypropanal ($CH(=O)CH_2CH_2OH$), and 4-hydroxybutanal ($CH(=O)CH_2CH_2CH_2OH$) were observed in the PFBHA derivatization experiments from the 2-butoxyethanol/$NO_3^\bullet$ reaction. The radical $CH_3CH_2CH_2CH_2OCH(^\bullet)CH_2(OH)$ is formed by hydrogen abstraction (position B on Structure 1) of the molecule as seen in Fig. 3. The radical reacts with oxygen to form the peroxyradical, $CH_3CH_2CH_2CH_2OCH(OO)(^\bullet)CH_2(OH)$. This species then dissociates to form $(^\bullet)(OO)CHCH_2(OH)$ and $CH_3CH_2CH_2CH_2O(^\bullet)$. The $(^\bullet)(OO)CHCH_2(OH)$ radical can further react with a RO molecule to form RO_2 and $CH(=O)CH_2OH$. The $CH_3CH_2CH_2CH_2O(^\bullet)$

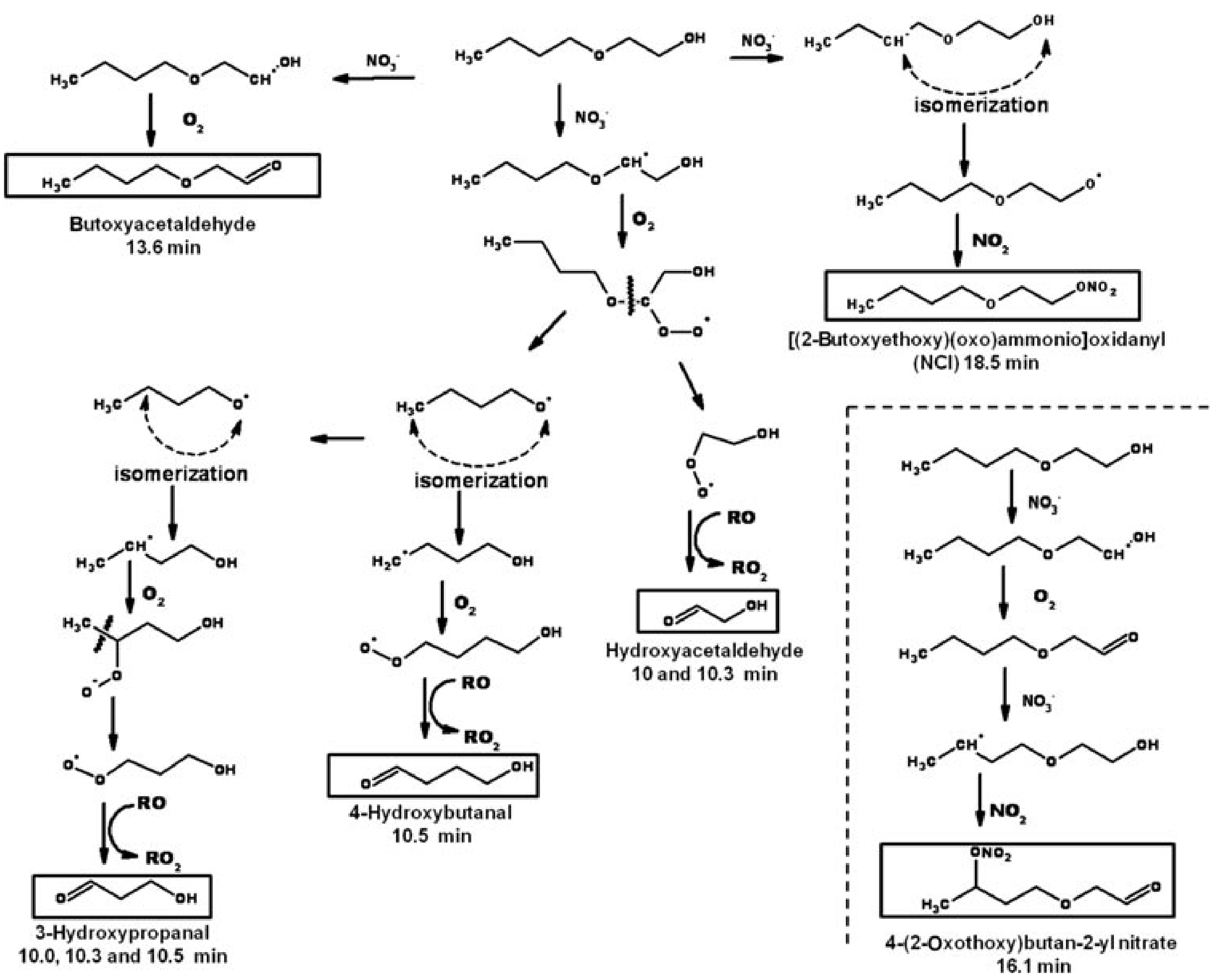


Figure 3 Proposed reaction mechanisms for observed products with 2-butoxyethanol and NO$_3^\bullet$.

radical isomerizes to form $CH_3CH(^\bullet)CH_2CH_2OH$ or $(^\bullet)CH_2CH_2CH_2CH_2OH$. The $CH_3CH(^\bullet)CH_2CH_2OH$ radical reacts with oxygen to form the peroxyradical, $CH_3CH(OO)(^\bullet)CH_2CH_2OH$ and then loses a CH_3 group. The $CH(OO)(^\bullet)CH_2CH_2OH$ radical can further react with a RO molecule to form RO_2 and $CH({=}O)CH_2CH_2OH$. The $(^\bullet)CH_2CH_2CH_2CH_2OH$ radical reacts with oxygen to form the peroxyradical, $(^\bullet)(OO)CH_2CH_2CH_2CH_2OH$. This can further react with a RO molecule to form RO_2 and $CH({=}O)CH_2CH_2CH_2OH$.

Oximes at Retention Time of 13.6 and 16.1 min. The oximes proposed as butoxyacetaldehyde ($CH_3CH_2CH_2CH_2OCH_2CH({=}O)$) and 4-(2-oxoethoxy)butan-2-yl nitrate ($CH_3CH(NO_2)CH_2CH_2OCH_2CH({=}O)$) were observed in the PFBHA derivatization experiments from the 2-butoxyethanol/NO$_3^\bullet$ reaction. The radical $CH_3CH_2CH_2CH_2OCH_2CH(^\bullet)(OH)$ is formed by hydrogen abstraction (position A on Structure 1) of the molecule as seen in Fig. 3. This then reacts with O_2 to give $CH_3CH_2CH_2CH_2OCH_2CH({=}O)$ and HO_2. The $CH_3CH_2CH_2CH_2OCH_2CH({=}O)$ molecule can react with another NO$_3^\bullet$ to form $CH_3CH(^\bullet)CH_2CH_2OCH_2CH({=}O)$. This then reacts with NO_2 to form $CH_3CH(NO_2)CH_2CH_2OCH_2CH({=}O)$.

Benzyl Alcohol/ NO$_3^\bullet$ PFBHA Reaction Products

Benzaldehyde Retention Time of 17.2 and 17.5 Min. Benzaldehyde ($C_6H_5C({=}O)H$) was the only product observed in the PFBHA derivatization experiments from the benzyl alcohol/NO$_3^\bullet$ reaction. The radical $(C_6H_5)CH(^\bullet)(OH)$ is formed by hydrogen abstraction of the alkyl hydrogen (position A on Structure 2) and a subsequent reaction with O_2 to give $C_6H_5C({=}O)H$ and HO_2 (see Fig. 4).

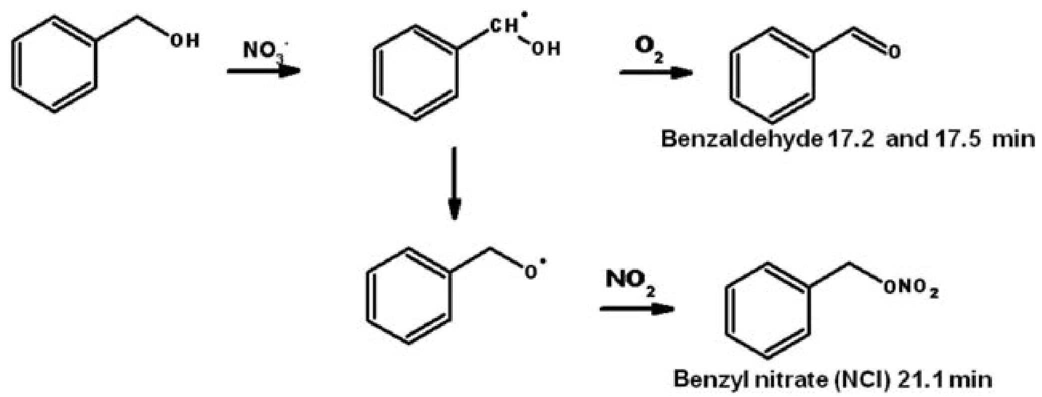


Figure 4 Proposed reaction mechanisms for observed products with benzyl alcohol and $NO_3^{\bullet}$.

2-Butoxyethanol/$NO_3^{\bullet}$ and Benzyl Alcohol/$NO_3^{\bullet}$ Nitrate Reaction Products

The 2-butoxyethanol/$NO_3^{\bullet}$ reaction product proposed as [(2-butoxyethoxy)(oxido) amino]oxidanide ($CH_3CH_2CH_2CH_2OCH_2CH_2ONO_2$) was detected using NCI. The radical $CH_3CH_2CH(^{\bullet})CH_2OCH_2CH_2OH$ is formed by hydrogen abstraction (position C on Structure 1) of the 2-butoxyethanol molecule as seen in Fig. 3. The radical then isomerizes to form $CH_3CH_2CH_2CH_2OCH_2CH_2O(^{\bullet})$ and then adds NO_2 to form $CH_3CH_2CH_2CH_2OCH_2CH_2ONO_2$.

The benzyl alcohol/$NO_3^{\bullet}$ reaction product proposed as benzyl nitrate ($(C_6H_5)CH_2ONO_2$) was detected using NCI. The radical $(C_6H_5)CH(^{\bullet})(OH)$ is formed by hydrogen abstraction (position A on Structure 2) of the alkyl hydrogen (see Fig. 4). This rearranges via a hydrogen shift to $(C_6H_5)CH_2O(^{\bullet})$, then adds NO_2 to form $(C_6H_5)CH_2ONO_2$.

To investigate the role NO_2 plays in the formation of benzyl nitrate, experiments were conducted using 2 ppm NO_2 and 0.75 ppm of either benzyl alcohol or benzaldehyde in a 65-L reaction chamber using very similar procedure as described above. The NCI system was employed to determine the possible products. These experiments did not lead to the formation of any detectable benzyl nitrate. Therefore, the benzyl nitrate formation pathway is dependent on the presence of $NO_3^{\bullet}$ and the formation of the alkoxy radical ($(C_6H_5)CH_2O(^{\bullet})$).

Atmospheric Implications in Indoor Air

An indoor environment nitrate radical concentration of 2×10^7 molecules/ cm^{-3} (approximately 1.1 ppt) has been previously estimated by Sarwar et al. [1]. Recently indoor nitrate radical concentrations of 1–58 ppt have been measured [31]. Using the 2-butoxyethanol/benzyl alcohol + $NO_3^{\bullet}$ rate coefficients reported here, a pseudo–first-order rate coefficient (k') of 0.0002–0.01 h^{-1} and 0.0003–0.017 h^{-1}, respectively, was determined. A comparison of this value to a typical indoor air exchange rate of 0.6 h^{-1} [4] suggests that air exchange is the most likely removal mechanism for 2-butoxyethanol and benzyl alcohol in the indoor environment. However, surface reactions may be important due to the fact that both compounds are large volume solvents and cleaners and can be applied to surfaces repeatedly.

An Agilent NCI GC/MS system provides the capability to analyze reaction products directly without the use of derivatization agents. This system can detect organic nitrates, which may be important components in indoor air. Some specific organic nitrates such peroxyacyl nitrates have demonstrated the potential to cause a number of adverse health effects including asthma, respiratory irritation, and is possibly a carcinogen [32,33]. It is anticipated that a number of organic nitrate compounds may be present in indoor air, may have harmful health effects, and should be investigated further [34].

DISCLAIMER

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/the Agency for Toxic Substances and Disease Registry.

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