Kinetics of the Gas-Phase Reactions of OH and NO_3 Radicals and O_3 with 1,4-Thioxane and 1,4-Dithiane

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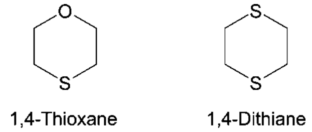
Rate constants for the gas-phase reactions of the cyclic organosulfur compounds 1,4-thioxane and 1,4-dithiane with NO_3 radicals and O_3 have been measured at 296 ± 2 K, and rate constants for their reactions with OH radicals have been measured over the temperature range 278−350 K. Relative rate methods were used to measure rate constants for the OH radical and NO_3 radical reactions. The OH radical reaction in the presence of NO_x and, to a lesser extent, the NO_3 radical reaction were subject to secondary reactions leading to additional removal of 1,4-thioxane and/or 1,4-dithiane. The rate constants obtained for the NO_3 radical and O_3 reactions at 296 ± 2 K were $(5.1 \pm 1.1) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} and $<2 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1}, respectively, for 1,4-thioxane and $(5.9 \pm 1.8) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} and $<2.5 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1}, respectively, for 1,4-dithiane. For the OH radical reactions, the temperature-dependent rate expressions obtained were $k(\text{OH} + \text{1,4-thioxane}) = 2.54 \times 10^{-12} e^{(619\pm51)/T}$ cm^3 molecule^{-1} s^{-1} (278−349 K) and $k(\text{OH} + \text{1,4-dithiane}) = 3.71 \times 10^{-12} e^{(621\pm163)/T}$ cm^3 molecule^{-1} s^{-1} (278−350 K), with 298 K rate constants of $(2.03 \pm 0.41) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for 1,4-thioxane and $(2.98 \pm 0.75) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for 1,4-dithiane. For the experimental conditions employed, aerosol formation from the OH radical-initiated reactions of both 1,4-thioxane and 1,4-dithiane was important, accounting for ~60% of the organosulfur compounds reacted in both the presence and absence of NO_x. The data obtained here for 1,4-thioxane and 1,4-dithiane are compared with literature data for the corresponding reactions of simple acyclic alkyl sulfides and ethers.

Introduction

Volatile organic compounds emitted into the atmosphere are generally removed from the troposphere by one or more of a series of chemical processes, including photolysis at wavelengths ≥290 nm, reaction with OH radicals, reaction with NO_3 radicals, and reaction with O_3.[1] Organosulfur compounds are emitted into the atmosphere mainly from natural sources,[2,3] and to date most studies of the atmospheric chemistry of organosulfur compounds have dealt with simple acyclic alkyl thiols (RSH) and alkyl sulfides (RSR′).[3−12] Kinetic studies show that daytime reaction with OH radicals and evening and nighttime reaction with NO_3 radicals are the dominant atmospheric transformation processes for the alkyl thiols and alkyl sulfides.[3,6,12] Tetrahydrothiophene is the only saturated cyclic sulfide studied to date, with measurements of its OH radical reaction rate constant having been reported.[4,13]

In order to extend the available database for alkyl sulfides to additional cyclic analogues, in this work we have measured rate constants for the gas-phase reactions of two cyclic sulfur-containing compounds, 1,4-thioxane and 1,4-dithiane, with OH radicals over the temperature range 278−350 K, and with NO_3 radicals and O_3 at room temperature. These two cyclic sulfur-containing compounds are analogues to 1,4-dioxane, with the two O-atoms in 1,4-dioxane being successively replaced by S-atoms.



Experimental Methods

Experiments to measure the OH and NO_3 radical and O_3 reaction rate constants were conducted at 296 ± 2 K and 735 Torr total pressure of dry purified air in a ~7000 L volume Teflon chamber,[14] equipped with two parallel banks of blacklamps for irradiation. Temperature-dependent experiments were carried out using a ~5000 L volume Teflon bag inserted inside a 5870 L Teflon-coated chamber, with irradiation provided by the 24-kW xenon arc lamp filtered through a 6 mm thick Pyrex pane to remove wavelengths <300 nm.[14,15] The 5870 L volume Teflon-coated evacuable chamber is fitted with a heating/cooling system, allowing its temperature to be maintained to within ±1 K over the range ~275−350 K.[14,15] Both chambers are fitted with Teflon-coated fans to ensure rapid mixing of reactants during their introduction into the chamber. Temperatures of the gas mixtures inside the chambers were measured by thermocouples, and in all experiments any temperature rise due to intermittent irradiations was ≤1 K.

Rate constants for the reactions of OH and NO_3 radicals with 1,4-thioxane and 1,4-dithiane were measured using relative rate techniques in which the concentrations of the organosulfur compound and a reference compound (whose OH or NO_3 radical reaction rate constant is reliably known) were measured in the presence of OH or NO_3 radicals.[14]

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$$\left.\begin{matrix}\mathrm{OH}\\ \mathrm{NO_3}\end{matrix}\right\} + \text{organosulfur compound} \rightarrow \text{products} \qquad (1)$$

$$\left.\begin{matrix}\mathrm{OH}\\ \mathrm{NO_3}\end{matrix}\right\} + \text{reference compound} \rightarrow \text{products} \qquad (2)$$

Providing that the organosulfur compound and the reference compound reacted only with OH or NO_3 radicals, then,

$$\ln\left(\frac{[\text{organosulfur}]_{t_0}}{[\text{organosulfur}]_t}\right) - D_t = \frac{k_1}{k_2}\left[\ln\left(\frac{[\text{reference compound}]_{t_0}}{[\text{reference compound}]_t}\right) - D_t\right] \qquad (\mathrm{I})$$

where $[\text{organosulfur}]_{t_0}$ and $[\text{reference compound}]_{t_0}$ are the concentrations of the organosulfur compound and reference compound, respectively, at time t_o, $[\text{organosulfur}]_t$ and $[\text{reference compound}]_t$ are the corresponding concentrations at time t, D_t is a factor to account for dilution caused by any additions to the chamber during the experiments ($D_t = 0$ for the OH radical reactions and $D_t = 0.0027$ per N_2O_5 addition to the chamber in the NO_3 radical reactions), and k_1 and k_2 are the rate constants for reactions 1 and 2, respectively.

Nitrate radicals were produced from the thermal decomposition of N_2O_5,[14] and NO_2 was also included in the reactant mixtures. The initial reactant concentrations (molecule cm^{-3}) were: 1,4-thioxane or 1,4-dithiane, and *trans*-2-butene, 1-butene, or thiophene (the reference compounds), $\sim 2.4 \times 10^{13}$ each; NO_2, $(2.4-4.8) \times 10^{13}$; and 2−3 additions of N_2O_5 (each addition corresponding to $(1.1-11.4) \times 10^{13}$ molecule cm^{-3} of N_2O_5 in the chamber) were made to the chamber during an experiment. The concentrations of organosulfur compound and reference compounds were measured during the experiments by gas chromatography with flame ionization detection (GC-FID), as described below.

OH radicals were generated in the presence of NO by the photolysis of methyl nitrite in the presence of O_2 at wavelengths >300 nm[14,15] or from the dark reaction of O_3 with 2-methyl-2-butene.[16] When OH radicals were generated by the photolysis of methyl nitrite, the initial reactant concentrations (molecule cm^{-3}) employed were: CH_3ONO, $\sim 2.4 \times 10^{14}$; NO, $\sim 2.4 \times 10^{14}$; and organosulfur compound and 1,3,5-trimethylbenzene (the reference compound), $\sim 2.4 \times 10^{13}$ each. Irradiations were carried out at 296 ± 2 K in the ~7000 L Teflon chamber for up to 60 min. While most experiments were carried out in air (21% O_2 content), experiments were also carried out at ~1%, ~6%, and ~78% O_2 content. An experiment was also carried out with dimethyl sulfide present in the reactant mixtures at an initial concentration of 2.4×10^{14} molecule cm^{-3}. NO and initial NO_2 concentrations were monitored using a Thermo Environmental Instruments, Inc., NO-NO_2-NO_x analyzer.

When the dark reaction of O_3 with 2-methyl-2-butene was used to generate OH radicals in the absence of NO_x, the initial concentrations (molecule cm^{-3}) were: organosulfur compound and di-*n*-butyl ether, 1,2,4- or 1,3,5-trimethylbenzene or triethyl phosphate (the reference compounds), $\sim 2.4 \times 10^{13}$ each; 2-methyl-2-butene, 4.5×10^{13}; and 3 additions of 100 cm^3 aliquots of O_3 in O_2 (each addition corresponding to $\sim 1.2 \times 10^{13}$ molecule cm^{-3} of O_3 in the chamber) were made to the chamber during the experiment. Experiments were carried out in air diluent, with one experiment at 296 ± 2 K for each organosulfur compound also being carried out in $N_2 + O_2$ diluent with ~78% O_2 content.

Experiments were also conducted to investigate the importance of dark decay and photolysis of $\sim 2.4 \times 10^{13}$ molecule cm^{-3} each of 1,4-thioxane and 1,4-dithiane in the chamber, with 1.6×10^{16} molecule cm^{-3} of cyclohexane being present in the photolysis experiment to scavenge any OH radicals formed during the 60 min of photolysis.

The concentrations of 1,4-thioxane and 1,4-dithiane and the reference compounds were measured during the experiments by GC-FID. For the analyses of 1-butene and *trans*-2-butene, gas samples were collected from the chamber into 100 cm^3 volume all-glass gastight syringes and transferred via a 1 cm^3 gas sampling loop onto a 30 m DB-5 megabore column initially held at −25 °C and then temperature programmed to 200 at 8 °C min^{-1}. For the analyses of thiophene, di-*n*-butyl ether, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, triethyl phosphate, 1,4-thioxane, and 1,4-dithiane, 100 cm^3 volume gas samples were collected from the chamber onto Tenax-TA solid adsorbent, with subsequent thermal desorption at ~205 °C onto a 30 m DB-1701 megabore column, initially held at −40 or 0 °C and then temperature programmed to 200 at 8 °C min^{-1}. On the basis of replicate analyses in the chamber in the dark, the analytical uncertainties for the organosulfur compounds and reference compounds were typically ≤3%.

The rate constants, or upper limits thereof, for the reactions of 1,4-thioxane and 1,4-dithiane with O_3 were determined by monitoring the decay of the organosulfur compound in the presence of a known concentration of O_3,[14] with cyclohexane being present to scavenge any OH radicals formed. Assuming that under these conditions the only loss process for the organosulfur compound was by reaction with O_3, then

$$\ln([\text{organosulfur}]_{t_0}/[\text{organosulfur}]_t) - D_t = k_3[O_3](t - t_0) \qquad (\mathrm{II})$$

where $[\text{organosulfur}]_{t_0}$ and $[\text{organosulfur}]_t$ are the concentrations of 1,4-thioxane or 1,4-dithiane at times t_o and t, respectively, D_t (= 0.0025) is the small amount of dilution caused by the initial addition of O_3 to the chamber, and k_3 is the rate constant for reaction 3.

$$O_3 + \text{organosulfur compound} \rightarrow \text{products} \qquad (3)$$

The initial reactant concentrations (molecule cm^{-3}) were 1,4-thioxane or 1,4-dithiane, $\sim 2.4 \times 10^{13}$; O_3, $(2.59-4.80) \times 10^{13}$; and cyclohexane, 1.6×10^{16}. O_3 concentrations were measured during the ~5.0 h duration reactions by ultraviolet absorption using a Dasibi Model 1003-AH ozone analyzer, and the concentrations of 1,4-thioxane and 1,4-dithiane were measured by GC-FID as described above.

Aerosol Formation. Aerosol formation was measured during CH_3ONO−NO−air irradiations of 1,4-thioxane and 1,4-dithiane and in the dark O_3 + 2-methyl-2-butene reactions of 1,4-thioxane, 1,4-dithiane, 1,4-thioxane + di-*n*-butyl ether, 1,4-dithiane + 1,3,5-trimethylbenzene, and 1,3,5-trimethylbenzene. These experiments were carried out in the ~7000 L Teflon chamber at 296 ± 2 K. The initial reactant concentrations and experimental procedures were as in the kinetic experiments, with three irradiation periods or three additions of O_3 in O_2 and with GC-FID analyses of the organosulfur compound and (if present) reference compound before and after each reaction period. The aerosol number density and size distribution were measured during the experiments using a TSI 3936L72 scanning mobility particle sizer (SMPS).

Chemicals. The chemicals used and their stated purities were di-*n*-butyl ether (99+%), 1,4-dithiane (97%), thiophene (99+%), 1,4-thioxane (98%), 1,2,4-trimethylbenzene (98%), and 1,3,5-trimethylbenzene (98%), Aldrich; 1-butene (≥99%), Liquid

TABLE 1: Rate Constant Ratios k_1/k_2 and Rate Constants k_1 (cm^3 molecule^{-1} s^{-1}) for the Reactions of NO_3 Radicals with 1,4-Thioxane, 1,4-Dithiane, and 1-Butene at 296 ± 2 K

		1,4-thioxane + 1,4-dithiane[a]		1,4-thioxane or 1,4-dithiane[b]	
reactant	reference compound	k_1/k_2[c]	$10^{14} \times k_1$[d]	k_1/k_2[c]	$10^{14} \times k_1$[d]
1,4-thioxane	*trans*-2-butene[e]	0.112 ± 0.022	4.36 ± 0.86		
	1-butene	4.38 ± 0.49	5.78 ± 0.65		
	thiophene	1.14 ± 0.09	4.48 ± 0.36	1.29 ± 0.04	5.07 ± 0.16[f]
1,4-dithiane	*trans*-2-butene[e]	0.135 ± 0.026	5.25 ± 1.02		
	1-butene	8.26 ± 1.25	10.9 ± 1.7		
	thiophene	1.92 ± 0.21	7.55 ± 0.83	1.51 ± 0.09	5.93 ± 0.36[f]
1-butene	thiophene			0.0316 ± 0.020	1.24 ± 0.08

[a] Experiments in which 1,4-thioxane and 1,4-dithiane were both present in the reactant mixtures. [b] Experiments in which 1,4-thioxane or 1,4-dithiane were studied separately. [c] Indicated errors are two least-squares standard deviations. [d] Placed on an absolute basis by use of a rate constants at 296 K of $k_2(NO_3 + trans\text{-}2\text{-butene}) = 3.89 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1},[1] $k_2(NO_3 + 1\text{-butene}) = 1.32 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1},[1] and $k_2(NO_3 + \text{thiophene}) = 3.93 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.[17] The indicated errors are the two least-squares standard deviations and do not include the uncertainties in the rate constant k_2. [e] From single experiment. [f] Estimated overall uncertainties are ±20% for 1,4-thioxane and ±30% for 1,4-dithiane (see text).

Carbonic; and NO (≥99.0%) and *trans*-2-butene (>95%), Matheson Gas Products. Methyl nitrite and N_2O_5 were prepared and stored as described elsewhere,[14] and O_3 in O_2 diluent was generated using a Welsbach T-408 ozone generator. NO_2 was prepared as needed by reacting NO with an excess of O_2.

Results

Photolysis and Dark Reactions. No decays (<5%) of 1,4-thioxane or 1,4-dithiane were observed in the ~7000 L Teflon chamber in the dark over a period of 5.3 h nor over a total period of 3.3 h during which four 15-min periods of irradiations were conducted at the same light intensity and spectral distribution as used in the OH radical rate constant determinations in the same chamber. These results show that dark losses and any photolysis of 1,4-thioxane and 1,4-dithiane were negligible under these conditions.

Rate Constants for Reactions with O_3. The gas-phase concentrations of 1,4-thioxane and 1,4-dithiane were measured in the ~7000 L Teflon chamber in the presence of average O_3 concentrations of 2.28×10^{13} molecule cm^{-3} and 4.45×10^{13} molecule cm^{-3}, with sufficient cyclohexane being present to scavenge >98% of any OH radicals formed. In each case, slow decays of 1,4-thioxane and 1,4-dithiane were observed, together with a decay of O_3 faster than that measured in the absence of added 1,4-thioxane or 1,4-dithiane. Thus, the background O_3 decay rate was measured to be 0.02 h^{-1}, while during the experiments the O_3 decay rates over periods of ~5.0 h were 0.034 h^{-1} (4.45×10^{13} molecule cm^{-3} O_3) and 0.054 h^{-1} (2.28×10^{13} molecule cm^{-3} O_3). Over the 5.0−5.1 h duration of the reactions, the measured concentrations of 1,4-thioxane decayed by ~5.6% and ~7.2% at average O_3 concentrations of 2.28×10^{13} molecule cm^{-3} and 4.45×10^{13} molecule cm^{-3}, respectively, while the corresponding 1,4-dithiane decays were ~8.7% and ~10.9%, respectively. Least-squares analyses of the experimental data using eq II lead to rate constants at 296 ± 2 K of $k(O_3 + 1,4\text{-thioxane}) \sim 7.5 \times 10^{-20}$ cm^3 molecule^{-1} s^{-1} and $k(O_3 + 1,4\text{-dithiane}) \sim 1.1 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1}, both with estimated overall uncertainties of ± 50%. Because of the low magnitude of these rate constants and the small amounts of 1,4-thioxane and 1,4-dithiane reacted, it is possible that the observed decays of gas-phase 1,4-thioxane and 1,4-dithiane were due to a slow reaction with O_3 at the chamber walls and hence that upper limits to the rate constants at 296 ± 2 K for gas-phase reactions of $<2 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} for 1,4-thioxane and $<2.5 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1} for 1,4-dithiane are more appropriate.

Rate Constants for Reactions with NO_3 Radicals. Reactions of N_2O_5−NO_3−NO_2−1,4-thioxane−reference compound−air, N_2O_5−NO_3−NO_2−1,4-dithiane−reference compound−air, and N_2O_5−NO_3−NO_2−1,4-thioxane−1,4-dithiane−reference compound−air mixtures were carried out at 296 ± 2 K in the ~7000 L Teflon chamber, with GC-FID analyses of 1,4-thioxane, 1,4-dithiane, and the reference compounds. Initial experiments had 1,4-thioxane and 1,4-dithiane both present in the reactant mixtures, and one experiment was carried out with *trans*-2-butene as the reference compound and three experiments with 1-butene as the reference compound. The rate constant ratios k_1/k_2 and rate constants k_1 obtained are given in Table 1 and indicate that the rate constants for the reactions of NO_3 radicals with 1,4-thioxane and 1,4-dithiane are in the range ~(4.4−5.8) $\times 10^{-14}$ cm^3 molecule^{-1} s^{-1} and ~(5.3−11) $\times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, respectively. All further experiments employed thiophene as the reference compound because its rate constant of 3.93×10^{-14} cm^3 molecule^{-1} s^{-1} at 296 K[17] is similar to those derived for 1,4-thioxane and 1,4-dithiane. Furthermore, in contrast to *trans*-2-butene and 1-butene, thiophene could be analyzed using the same sample collection procedure and GC column as 1,4-thioxane and 1,4-dithiane, thereby minimizing errors associated with the measurement procedure. After two experiments in which both 1,4-thioxane and 1,4-dithiane were present in the reactant mixtures, experiments were carried out with 1,4-thioxane and 1,4-dithiane being studied separately. As evident from Table 1, experiments in which 1,4-thioxane and 1,4-dithiane were studied separately yielded somewhat different rate constant ratios than when both compounds were present in the same experiments. Furthermore, when both 1,4-thioxane and 1,4-dithiane were present in the reactant mixtures, there were experiment-to-experiment differences in the three experiments with 1-butene and the two experiments with thiophene as the reference compound, as well as inconsistencies between experiments with different reference compounds (Table 1). This behavior suggests that some secondary chemistry occurs, being most evident for 1,4-dithiane when both organosulfur compounds are present together.

Rate constants were therefore determined from experiments using thiophene as the reference compound and with 1,4-thioxane and 1,4-dithiane being studied separately. 1-Butene was also included in the reactant mixtures in several of these experiments, and two of these experiments (one each for 1,4-thioxane and 1,4-dithiane) were carried out in $N_2 + O_2$ diluent gas with ~75% (1,4-thioxane) or ~78% (1,4-dithiane) O_2 content. The experimental data from experiments in which 1,4-

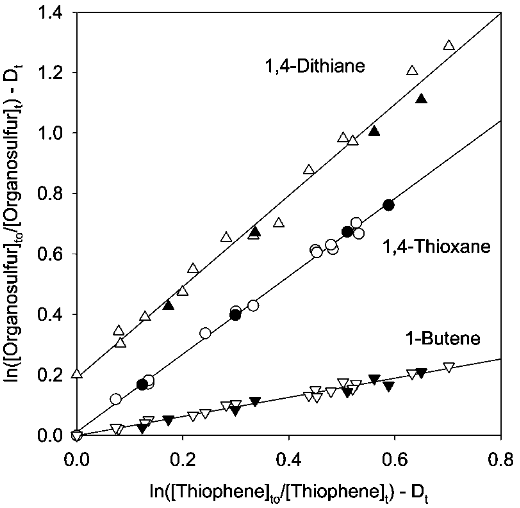

Figure 1. Plots of eq 1 for the reaction of NO$_3$ radicals with 1,4-thioxane, 1,4-dithiane, and 1-butene at 296 ± 2 K, with thiophene as the reference compound. ○, △, ▽: experiments in air; ●, ▲, ▼: experiments in N$_2$ + O$_2$ with O$_2$ contents of ~75% (1,4-thioxane) or ~78% (1,4-dithiane). 1,4-Thioxane and 1,4-dithiane were studied separately, and the data for 1,4-dithiane have been displaced vertically by 0.20 units for clarity.

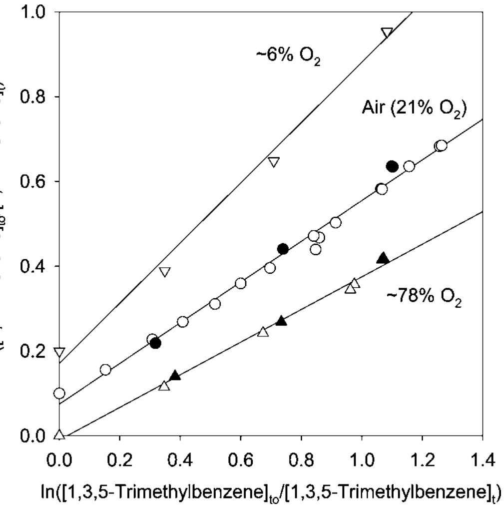

Figure 2. Plots of eq 1 for the reaction of OH radicals with 1,4-thioxane at 296 ± 2 K, with 1,3,5-trimethylbenzene as the reference compound. OH radicals were generated by the photolysis of CH$_3$ONO in air in the presence of NO. ○, △, ▽: experiments with 1,4-thioxane and 1,4-dithiane both present in the reactant mixtures; ●, ▲: experiments in which 1,4-thioxane was studied alone. The data for 1,4-thioxane at 21% O$_2$ and at ~6% O$_2$ have been displaced vertically by 0.10 and 0.20 units, respectively, for clarity.

thioxane and 1,4-dithiane were studied separately are plotted in accordance with eq 1 in Figure 1. The plots are good straight lines, and the data at ~75−78% O$_2$ content were indistinguishable from those in air. The rate constant ratios k_1/k_2 obtained from least-squares analyses of the data in Figure 1 are given in Table 1, together with rate constants k_1 derived using a rate constant at 296 K of k_2(NO$_3$ + thiophene) = 3.93×10^{-14} cm^3 molecule^{-1} s^{-1}.[17] The rate constant for 1-butene, of $(1.24 \pm 0.08) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 296 ± 2 K, is in excellent agreement with the recommended value at 296 K of 1.32×10^{-14} cm^3 molecule^{-1} s^{-1}.[1] Clearly, the rate constants measured for 1,4-thioxane and 1,4-dithiane when studied separately could still be subject to secondary reactions, and the overall uncertainties of these rate constants are estimated to be ±20% for 1,4-thioxane and ±30% for 1,4-dithiane, with k(NO$_3$ + 1,4-thioxane) = $(5.1 \pm 1.1) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 296 ± 2 K, and k(NO$_3$ + 1,4-dithiane) = $(5.9 \pm 1.8) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 296 ± 2 K.

Rate Constants for Reactions with OH Radicals at 296 ± 2 K. A series of experiments was carried out at 296 ± 2 K in the ~7000 L Teflon chamber, using both the photolysis of methyl nitrite in air in the presence of NO and the dark reaction of O$_3$ with 2-methyl-2-butene to generate OH radicals. 1,3,5-Trimethylbenzene was used as the reference compound in all cases. Irradiations of CH$_3$ONO−NO−1,4-thioxane−1,4-dithiane−1,3,5-trimethylbenzene−air (or N$_2$ + O$_2$ diluent) mixtures were conducted at O$_2$ contents of ~1%, ~6%, 21% (air) and ~78%. As noted previously,[18] because of the competition between reactions 4, 5 and 6,

$$CH_3O^\bullet + O_2 \rightarrow HCHO + HO_2 \qquad (4)$$

$$CH_3O^\bullet + NO + M \rightarrow CH_3ONO + M \qquad (5)$$

$$CH_3O^\bullet + NO + M \rightarrow CH_3ONO_2 + M \qquad (6)$$

in air in the presence of 2.4×10^{14} molecule cm^{-3} of NO + NO$_2$, each CH$_3$O$^\bullet$ radical formed from photolysis of CH$_3$ONO results in the formation of ~0.6−0.7 HO$_2$ radicals (and hence OH radicals).[12] Reactions 5 and 6 become more important as the O$_2$ content decreases, and with the same initial CH$_3$ONO concentration and light intensity, the OH radical concentrations at ~78% O$_2$, ~6% O$_2$, and ~1% O$_2$ content, relative to that in air, are calculated to be ~1.3, ~0.55, and ~0.13, respectively. The OH radical concentrations derived from the 1,3,5-trimethylbenzene decay rates during the irradiations at the various O$_2$ contents were (in units of 10^6 molecule cm^{-3}) 16−17 in ~78% O$_2$, 10−11 in 21% O$_2$ (air), 5.3 in ~6% O$_2$, and 2.2 in ~1% O$_2$, in good relative agreement with expectations based solely on reactions 4, 5, and 6. When replicate experiments were carried out (in air and in ~78% O$_2$), the OH radical concentrations were very reproducible at a given O$_2$ content and were either essentially constant (over 60 min at 6% O$_2$) or decreased slightly (by ~15% over the 30−36 min irradiation periods in air) during the irradiations. Furthermore, the OH radical concentration in the presence of dimethyl sulfide was identical to those in its absence.

Figure 2 shows plots of eq 1 for the 1,4-thioxane reaction at ~6%, 21% (air), and ~78% O$_2$ content, and it is evident from Figure 2 and Table 2 that the measured rate constant ratios k_1/k_2 decrease with increasing O$_2$ content. This in contrast to the reaction of OH radicals with dimethyl sulfide, where at room temperature the measured rate constant increases with increasing O$_2$ concentration.[3,7,12] One explanation for this observed effect of O$_2$ on the measured rate constants for 1,4-thioxane and 1,4-dithiane is that the reactions of OH radicals with 1,4-thioxane and 1,4-dithiane form reactive S-containing radical intermediates which can react with 1,4-thioxane and 1,4-dithiane but not with 1,3,5-trimethylbenzene, and this radical intermediate also reacts with O$_2$ to form a nonreactive (toward 1,4-thioxane and 1,4-dithiane) species. In this case, the rate constant ratios at high O$_2$ concentration would be the rate constant for the initial step. However, it is surprising that the rate data are independent of whether or not both organosulfur compounds are present in the same experiment, although it is possible that there are differences but that they are less than the experimental errors.

It is possible that this reactive species is O(^{3}P) atoms, since varying the O$_2$ concentration of the diluent gas also had an effect on NO-to-NO$_2$ conversion and hence on O(^{3}P) atom production from NO$_2$ photolysis. NO-to-NO$_2$ conversion (as measured by

TABLE 2: Rate Constant Ratios k_1/k_2 for the Reaction of OH Radicals with 1,4-Thioxane and 1,4-Dithiane at 296 ± 2 K, with 1,3,5-Trimethylbenzene as the Reference Compound

O_2 content in diluent gas	OH generated from	k_1/k_2[a]	
		1,4-thioxane	1,4-dithiane
~1%	$CH_3ONO + h\nu$	0.991 ± 0.037[b]	1.53 ± 0.05[b]
~6%	$CH_3ONO + h\nu$	0.710 ± 0.064[b]	1.07 ± 0.08[b]
21% (air)	$CH_3ONO + h\nu$	0.480 ± 0.022[c]	0.679 ± 0.015[c]
21% (air) + DMS[d]	$CH_3ONO + h\nu$	0.592 ± 0.050[b]	0.946 ± 0.090[b]
21% (air)	O_3 + 2-methyl-2-butene	0.384 ± 0.013[e]	0.541 ± 0.022[e]
~78%	$CH_3ONO + h\nu$	0.385 ± 0.023[c]	0.554 ± 0.030[c]
~78%[d]	O_3 + 2-methyl-2-butene	0.393 ± 0.025[e]	0.544 ± 0.024[e]

[a] Indicated errors are 2 least-squares standard deviations. [b] From single experiment with both 1,4-thioxane and 1,4-dithiane present. [c] From experiments with 1,4-thioxane and 1,4-dithiane both present in the reactant mixtures and experiments in which 1,4-thioxane and 1,4-dithiane were studied separately (see also Figure 2). [d] With 2.4 × 10^{14} molecule cm^{-3} of dimethyl sulfide (DMS) included in the reactant mixture (see text). [e] From single experiment, with 1,4-thioxane and 1,4-dithiane being studied separately.

the decrease in NO concentrations during the reactions) decreased markedly as the O_2 content decreased, with measured decreases in the NO concentrations during the reactions (in units of 10^{13} molecule cm^3) of ~15 in ~78% O_2, ~11 in 21% O_2 (air), ~6 in ~6% O_2, and ~1 in ~1% O_2. Assuming these NO decreases were balanced by corresponding increases in NO_2,[19] then the final $O(^3P)$ atom concentrations would have increased by a factor of ~5 on decreasing the O_2 content from ~78% to ~6%. Assuming that 1,4-thioxane and 1,4-dithiane react with $O(^3P)$ atoms as rapidly as does dimethyl sulfide (5.0 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 298 K[12]), then the $O(^3P)$ atom reactions could have been of minor importance in air and of more importance as a loss process for 1,4-thioxane and 1,4-dithiane at the lower O_2 contents employed. If that were the case, the slopes of the plots of eq 1, such as those shown in Figure 2, should have increased significantly as the reactions proceeded (and as NO was converted to NO_2). While there is some evidence of positive curvature in these plots, the effects are small and in air (for which the most experiments were conducted using CH_3ONO photolysis as the OH radical source), the initial slopes of eq 1 are within 8% of those for the entire data set for both 1,4-thioxane and 1,4-dithiane. Figure 3 shows plots of the rate constant ratios k_1/k_2 against $1/[O_2]$, and it appears that when using CH_3ONO photolysis as the OH radical precursor the rate constant ratios at ~78% O_2 content are close to those from extrapolation to $1/[O_2] = 0$.

The reaction of OH radicals with dimethyl sulfide has also been shown to be subject to secondary reactions when experiments are conducted in the presence of NO_x,[20−22] presumably due to CH_3SO_x (possibly CH_3SO_3) radicals formed from CH_3S radicals.[3] An experiment was therefore carried out in air, with 2.4 × 10^{14} molecule cm^{-3} of dimethyl sulfide also included in the reactant mixture (the rate of reaction of OH radicals with dimethyl sulfide then being approximately the same as the sum of the rates of reaction of OH radicals with 1,4-thioxane and 1,4-dithiane). As seen from Table 2 and Figure 3, the inclusion of dimethyl sulfide significantly increased the measured rate constant ratios for both 1,4-thioxane and 1,4-dithiane, suggesting that these compounds are susceptible to secondary reactions from intermediate radicals formed from dimethyl sulfide. The increase in rate constant ratios k_1/k_2 in this experiment with added dimethyl sulfide does not appear to be due to $O(^3P)$ atom reaction, since the OH radical concentration was identical to that in the absence of dimethyl sulfide and the NO-to-NO_2 conversion increased only slightly compared to experiments without added dimethyl sulfide, resulting in an essentially unchanged $O(^3P)$ atom concentration because of the higher loss rate of $O(^3P)$ atoms in the presence of dimethyl sulfide. Hence, while it is possible that some of the observed increase in rate constant ratio with decreasing O_2 content when using CH_3ONO photolysis to generate OH radicals was due to the occurrence of $O(^3P)$ atom reactions, it also appears that secondary reactions of 1,4-thioxane and 1,4-dithiane with sulfur-containing radicals occurred in the presence of NO_x.

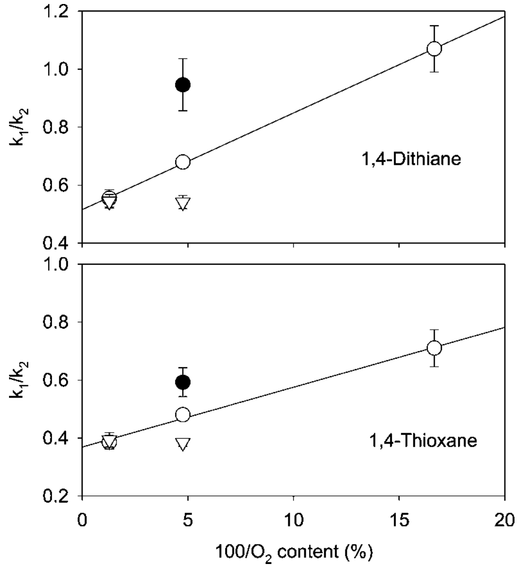

Figure 3. Plots of the measured rate constant ratios k_1/k_2 for the reactions of OH radicals with 1,4-thioxane and 1,4-dithiane at 296 ± 2 K (Table 2) against $1/[O_2]$. ○, ●: OH radicals generated by photolysis of CH_3ONO in the presence of NO; ●: with 2.4 × 10^{14} molecule cm^{-3} of dimethyl sulfide included in the reactant mixtures; ▽: OH radicals generated by the dark reaction of O_3 with 2-methyl-2-butene. The solid lines are least-squares fits to the data denoted by ○ (i.e., in the presence of NO_x without added dimethyl sulfide). Note that the scale of the *Y*-axis is the same for the two portions of the plot.

For the reaction of OH radicals with methyl sulfide, the effects of secondary reactions are observed only in the presence of NO_x,[20−22] and hence experiments were carried out in the absence of NO_x, with OH radicals being generated from the dark reaction of O_3 with 2-methyl-2-butene. 1,4-Thioxane and 1,4-dithiane were studied separately in these experiments in order to maximize the extents of reaction of each of the organosulfur compounds (production of OH radicals was limited by the amount of 2-methyl-2-butene reacted and the OH radicals reacted with 2-methyl-2-butene and the other compounds present in the reaction mixture), and experiments were carried out in air and in $N_2 + O_2$ diluent with ~78% O_2 content. The measured rate constant ratios are given in Table 2 and are plotted in Figure 3, and within the experimental uncertainties the measured rate

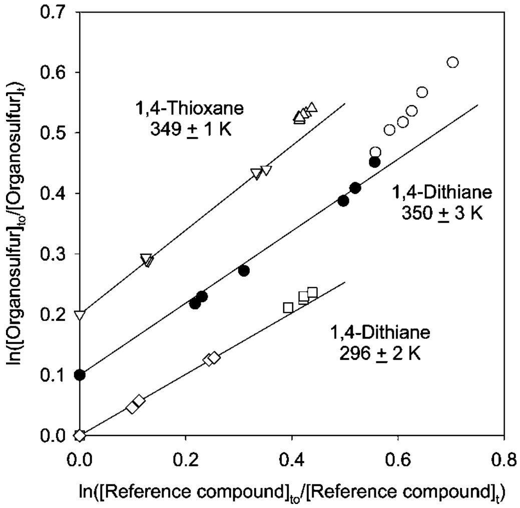

Figure 4. Representative plots of eq 1 for the reaction of OH radicals with 1,4-thioxane and 1,4-dithiane. The reference compounds were di-*n*-butyl ether for 1,4-thioxane at 349 ± 1 K (~5000 L Teflon bag) and 1,3,5-trimethylbenzene for 1,4-dithiane at 296 ± 2 K (in 21% and ~78% O_2 content diluent gas, ~7000 L Teflon chamber) and 350 ± 3 K (~5000 L Teflon bag). OH radicals were generated from the dark reaction of O_3 with 2-methyl-2-butene. ▽,●, ◇: data obtained after the first and second O_3 in O_2 additions; △, ○, □: data obtained after the third O_3 in O_2 addition (see text). Data for 1,4-thioxane and for 1,4-dithiane at 350 ± 3 K have been displaced vertically by 0.20 and 0.10 units, respectively, for clarity.

constant ratios at 21% and ~78% O_2 content were identical for both 1,4-thioxane and 1,4-dithiane and also essentially identical to the rate constant ratios measured at ~78% O_2 content using CH_3ONO photolysis to generate OH radicals.

Rate Constants for Reactions with OH Radicals over the Temperature Range 278−350 K. The above experiments at 296 ± 2 K suggest that in order to measure rate constants for the reactions of OH radicals with 1,4-thioxane and 1,4-dithiane which are free from secondary reactions, experiments need to be carried out either at high O_2 concentrations if the photolysis of CH_3ONO is used to generate OH radicals, or in the absence of NO_x. Rate constants were measured over the temperature range 278−350 K in a ~5000 L Teflon bag inserted inside a 5870 L thermostatted, evacuable chamber, and OH radicals were generated from the dark reaction of O_3 with 2-methyl-2-butene. As at 296 ± 2 K, experiments with 1,4-thioxane and 1,4-dithiane were conducted separately. Di-*n*-butyl ether was initially chosen as the reference compound because its room temperature OH radical reaction rate constant[23] is similar to those for 1,4-thioxane and 1,4-dithiane, and the temperature dependence of the rate constant for di-*n*-butyl ether is more accurately known that that for 1,3,5-trimethylbenzene.[15] However, because of coelution of a reaction product of di-*n*-butyl ether with 1,4-dithiane, 1,3,5-trimethylbenzene was used for experiments with 1,4-dithiane. Additional experiments were carried out at 350 ± 1 K for 1,4-thioxane with 1,3,5-trimethylbenzene and triethyl phosphate as the reference compounds, and at 300 ± 1 K and 350 ± 1 K for 1,4-dithiane with 1,2,4-trimethylbenzene and triethyl phosphate, respectively, as the reference compounds.

Representative plots of eq 1 are shown in Figure 4 for 1,4-thioxane at 350 ± 1 K and for 1,4-dithiane at 296 ± 2 K (in the ~7000 L Teflon chamber) and at 350 ± 3 K. It is evident, especially for the data for 1,4-dithiane at 350 K, that these plots exhibit curvature, with the slopes increasing at larger extents of reaction. In these experiments, after prereaction GC-FID analyses, three additions of O_3 in O_2 were made to the chamber, with GC-FID analyses after each addition and with one or more replicate analyses after the third addition (similarly, when CH_3ONO photolysis was used as OH radical source, three irradiations were carried out with GC-FID analyses after each and with a replicate after the third). In all cases (as evident from Figure 4), the data points after the third O_3 addition (or third irradiation) were largely responsible for the curvature in the plots of eq 1. Curvature was more apparent at higher and lower temperatures and was essentially absent for the experiments carried out in the ~7000 L chamber at 296 ± 2 K, as shown, for example, by the data in Figure 4 for 1,4-dithiane at 296 ± 2 K. Furthermore, curvature of plots of eq 1 was more pronounced for 1,4-dithiane than for 1,4-thioxane, as evident from Figure 4 from the 349−350 K data for 1,4-thioxane and 1,4-dithiane.

We used four methods to analyze these data at a given temperature and with a given reference compound: (A) a least-squares analysis of the entire data set, using one (0,0) point and not constraining the fit to pass through the origin; (B) the same data as A but constraining the least-squares fit to pass through the origin; (C) using the data points collected after the first two O_3/O_2 additions (or the first two irradiation periods), using one (0,0) point and not constraining the fit to pass through the origin; (D) the same data as C but constraining the least-squares fit to pass through the origin. The lines drawn through the sets of data in Figure 4 are method D, while those shown in Figure 2 used method A. Tables 3 and 4 give the rate constant ratios k(OH + 1,4-thioxane)/k(OH + reference compound) and k(OH + 1,4-dithiane)/k(OH + reference compound), respectively, for all four analysis procedures. As expected (for example, from Figure 4), for a given set of experiments the rate constant ratios decrease in the order of data analysis method A > B > C ~ D, with method A resulting in a negative intercept in all cases. Also, the differences between the different analysis methods A through D are less for 1,4-thioxane than for 1,4-dithiane (i.e., less curvature in the plots for 1,4-thioxane than for 1,4-dithiane) and are also less for the room temperature experiments, in part because of lower extents of reaction for those experiments at 296 ± 2 K in the ~7000 L Teflon chamber with OH radicals formed from the dark O_3 + 2-methyl-2-butene reaction. We prefer the analysis method D, the results of which are essentially identical to those from method C.

The rate constant ratios obtained using analysis method D are placed on an absolute basis using rate constants of k(OH + di-*n*-butyl ether) = $6.29 \times 10^{-18} T^2 e^{1164/T}$ cm^3 molecule^{-1} s^{-1},[23] k(OH + 1,3,5-trimethylbenzene) = $4.69 \times 10^{-12} e^{738/T}$ cm^3 molecule^{-1} s^{-1} (5.67×10^{-11} cm^3 molecule^{-1} s^{-1} at 296 K),[1,15] k(OH + 1,2,4-trimethylbenzene) = 3.25×10^{-11} cm^3 molecule^{-1} s^{-1} at ~298 K,[1] and k(OH + triethyl phosphate) = 2.55×10^{-11} cm^3 molecule^{-1} s^{-1} at 350 K.[15] The resulting rate constants k_1 are given in Table 5 and, apart from those obtained from single experiments at 350 ± 1 K using triethyl phosphate or 1,3,5-trimethylbenzene as the reference compounds, are plotted in Arrhenius form in Figure 5.

At room temperature, the rate constants measured for 1,4-thioxane and 1,4-dithiane with di-*n*-butyl ether and 1,3,5-trimethylbenzene (1,4-thioxane) and with 1,2,4- and 1,3,5-trimethylbenzene (1,4-dithiane) as the reference compounds are in excellent agreement. The rate constants obtained for 1,4-thioxane at 350 ± 1 K from a single experiment each with 1,3,5-trimethylbenzene and triethyl phosphate as the reference compounds are 15−20% higher than the rate constant measured relative to di-*n*-butyl ether at 349 ± 1 K, while the rate constant for 1,4-dithiane at 350 ± 1 K from a single experiment with

TABLE 3: Rate Constant Ratios k(OH + 1,4-thioxane)/k(OH + reference compound) at the Temperatures Studied Using the Data Analysis Methods Discussed in the Text[a]

		all data points		first two data points	
T (K)	reference compound	unconstrained(A)	through (0,0)(B)	unconstrained(C)	through (0.0)(D)
278 ± 1	DnBE	0.840 ± 0.065	0.797 ± 0.070	0.752 ± 0.022	0.738 ± 0.027
296 ± 2	1,3,5-TMB[b]	0.385 ± 0.023	0.373 ± 0.025	0.366 ± 0.021	0.361 ± 0.022
296 ± 2	1,3,5-TMB[c]	0.391 ± 0.016	0.383 ± 0.017	0.370 ± 0.034	0.368 ± 0.034
299 ± 1	DnBE	0.789 ± 0.036	0.761 ± 0.040	0.717 ± 0.014	0.716 ± 0.014
321 ± 1	DnBE	0.756 ± 0.098	0.732 ± 0.099	0.630 ± 0.152	0.656 ± 0.155
349 ± 1	DnBE	0.784 ± 0.052	0.759 ± 0.055	0.688 ± 0.026	0.697 ± 0.027
350 ± 1	TEP[d]	0.751 ± 0.063	0.732 ± 0.067	0.687 ± 0.037	0.679 ± 0.043
350 ± 1	1,3,5-TMB[d]	0.549 ± 0.095	0.530 ± 0.098	0.468 ± 0.009	0.470 ± 0.010

[a] Indicated errors are two least-squares standard deviations. OH radicals were generated by the dark reaction of O_3 with 2-methyl-2-butene unless noted otherwise. DnBE = di-*n*-butyl ether; TMB = trimethylbenzene; TEP = triethyl phosphate. [b] OH radicals were generated by photolysis of methyl nitrite in ~78% O_2 + ~22% N_2 mixtures in the presence of NO (see text and Figure 2). [c] From experiments in air and in ~78% O_2 + ~22% N_2 mixtures (see text). [d] From a single experiment.

TABLE 4: Rate Constant Ratios k(OH + 1,4-dithiane)/k(OH + reference compound) at the Temperatures Studied Using the Data Analysis Methods Discussed in the Text[a]

		all data points		first two points	
T (K)	reference compound	unconstrained(A)	through (0,0)(B)	unconstrained(C)	through (0,0)(D)
278 ± 1	1,3,5-TMB	0.652 ± 0.064	0.612 ± 0.069	0.557 ± 0.014	0.549 ± 0.016
283 ± 1	1,3,5-TMB	0.638 ± 0.059	0.600 ± 0.064	0.547 ± 0.011	0.540 ± 0.013
296 ± 2	1,3,5-TMB[b]	0.554 ± 0.030	0.545 ± 0.031	0.534 ± 0.035	0.530 ± 0.036
296 ± 2	1,3,5-TMB[c]	0.547 ± 0.016	0.533 ± 0.021	0.513 ± 0.023	0.507 ± 0.025
300 ± 1	1,2,4-TMB	0.979 ± 0.059	0.927 ± 0.068	0.864 ± 0.021	0.851 ± 0.025
321 ± 1	1,3,5-TMB	0.621 ± 0.039	0.593 ± 0.043	0.539 ± 0.006	0.542 ± 0.007
350 ± 3	1,3,5-TMB	0.736 ± 0.073	0.669 ± 0.086	0.618 ± 0.047	0.594 ± 0.053
350 ± 1	TEP[d]	0.938 ± 0.112	0.906 ± 0.118	0.820 ± 0.034	0.814 ± 0.037

[a] Indicated errors are two least-squares standard deviations. OH radicals generated by the dark reaction of O_3 with 2-methyl-2-butene unless noted otherwise. TMB = trimethylbenzene; TEP = triethyl phosphate. [b] OH radicals were generated by photolysis of methyl nitrite in ~78% O_2 + ~22% N_2 mixtures in the presence of NO (see text). [c] From experiments in air and in ~78% O_2 + ~22% N_2 mixtures (see text and Figure 4). [d] From a single experiment.

triethyl phosphate as the reference compound is 10% lower than that at 350 ± 3 K measured relative to 1,3,5-trimethylbenzene. This level of agreement is considered reasonable since only single experiments were carried out using triethyl phosphate and (for 1,4-thioxane) 1,3,5-trimethylbenzene, and the rate constants of triethyl phosphate and 1,3,5-trimethylbenzene at 350 K are uncertain to at least ± 12%.[15] Note that the rate constant ratio k(OH + triethyl phosphate)/k(OH + 1,3,5-trimethylbenzene) = 0.692 ± 0.047 at 350 ± 1 K (error is two standard deviations) derived from the separate rate constant ratios k(OH + 1,4-thioxane)/k(OH + triethyl phosphate) and k(OH + 1,4-thioxane)/k(OH + 1,3,5-trimethylbenzene) agrees well with the directly measured value of 0.735 ± 0.039 at 347 ± 2 K.[15]

Least-squares analyses of the rate constants for 1,4-thioxane (other than that at 321 ± 1 K which has a large associated uncertainty) and of those for 1,4-dithiane (Figure 5) result in the Arrhenius expressions $k(\mathrm{OH} + 1,4\text{-thioxane}) = 2.54 \times 10^{-12}\, e^{(619\pm51)/T}$ cm^3 molecule^{-1} s^{-1} (278−349 K), and $k(\mathrm{OH} + 1,4\text{-dithiane}) = 3.71 \times 10^{-12}\, e^{(621\pm163)/T}$ cm^3 molecule^{-1} s^{-1} (278−350 K), where the indicated errors are two least-squares standard deviations. These Arrhenius expressions are shown as the solid lines in Figure 5. The 298 K rate constants are then $k(\mathrm{OH} + 1,4\text{-thioxane}) = 2.03 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and $k(\mathrm{OH} + 1,4\text{-dithiane}) = 2.98 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, with estimated overall uncertainties of ±20% for 1,4-thioxane and ±25% for 1,4-dithiane. Analysis methods A and B led to Arrhenius fits with similar temperature dependencies and rate constants higher by 10−11% (method A) and 6% (method B) over the temperature range 278−349 K for 1,4-thioxane and

TABLE 5: Rate Constants k_1 (cm^3 molecule^{-1} s^{-1}) for the Reactions of OH Radicals with 1,4-Thioxane and 1,4-Dithiane[a]

	1,4-thioxane		1,4-dithiane	
temp (K)	reference	$10^{11} \times k_1$[b]	reference	$10^{11} \times k_1$[b]
278 ± 1	DnBE	2.36 ± 0.09	1,3,5-TMB	3.66 ± 0.11
283 ± 1			1,3,5-TMB	3.44 ± 0.09
296 ± 2	1,3,5-TMB	2.05 ± 0.13[c]	1,3,5-TMB	3.01 ± 0.21[c]
296 ± 2	1,3,5-TMB	2.09 ± 0.20[d]	1,3,5-TMB	2.87 ± 0.15[d]
299 ± 1	DnBE	1.98 ± 0.04		
300 ± 1			1,2,4-TMB	2.77 ± 0.09
321 ± 1	DnBE	1.60 ± 0.38	1,3,5-TMB	2.53 ± 0.04
349 ± 1	DnBE	1.50 ± 0.06		
350 ± 3			1,3,5-TMB	2.29 ± 0.21
350 ± 1	TEP	1.73 ± 0.11[e]	TEP	2.07 ± 0.10[e]
350 ± 1	1,3,5-TMB	1.82 ± 0.04[e]		

[a] Reference compounds: DnBE = di-*n*-butyl ether; TMB = trimethylbenzene; TEP = triethyl phosphate. OH radicals generated by the dark reaction of O_3 with 2-methyl-2-butene unless noted otherwise. [b] Rate constant ratios from Tables 3 and 4 (using method D; first two data points, fit constrained to pass through the origin) placed on an absolute basis by use of rate constants k_2(di-*n*-butyl ether) = $6.29 \times 10^{-18}\, T^2\, e^{1164/T}$ cm^3 molecule^{-1} s^{-1},[23] k_2(1,3,5-trimethylbenzene) = $4.69 \times 10^{-12}\, e^{738/T}$ cm^3 molecule^{-1} s^{-1} (5.67×10^{-11} cm^3 molecule^{-1} s^{-1} at 296 K),[1,15] k_2(1,2,4-trimethylbenzene) = 3.25×10^{-11} cm^3 molecule^{-1} s^{-1} at ~298 K,[1] and k_2(triethyl phosphate) = 2.55×10^{-11} cm^3 molecule^{-1} s^{-1} at 350 K.[15] The indicated errors are the two least-squares standard deviations and do not include the uncertainties in the rate constants k_2, which are likely to be ~ ± 10−12%. [c] OH radicals were generated by photolysis of methyl nitrite in ~78% O_2 + ~22% N_2 mixtures in the presence of NO (see text). [d] From experiments in air and in ~78% O_2 + ~22% N_2 mixtures (see text). [e] From a single experiment.

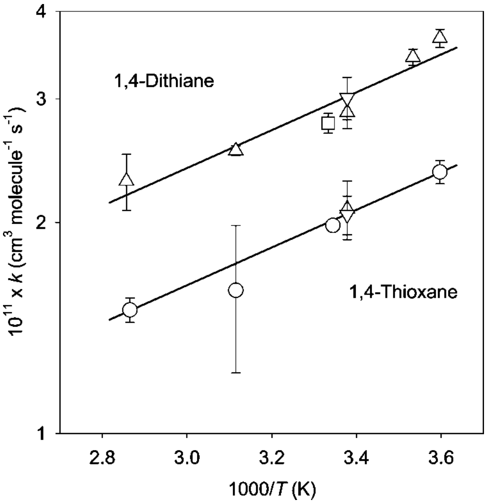

Figure 5. Arrhenius plots of the rate constants k_1 for the reactions of OH radicals with 1,4-thioxane and 1,4-dithiane. ○, Relative to di-*n*-butyl ether in the absence of NO$_x$; ▽, relative to 1,3,5-trimethylbenzene in the absence of NO$_x$; ▽, relative to 1,3,5-trimethylbenzene in the presence of NO$_x$; □, relative to 1,2,4-trimethylbenzene in the absence of NO$_x$.

higher by 12−19% (method A) and 8−10% (method B) over the temperature range 278−350 K for 1,4-dithiane.

Aerosol Formation from the OH Radical Reactions. Experiments were carried out in the ~7000 L Teflon chamber at 296 ± 2 K to measure aerosol formation, with the fraction of the initially present 1,4-thioxane and 1,4-dithiane reacted by the end of the experiments being 44% and 62% in the CH$_3$ONO−air irradiations, and 19−24% and 23−31% in the dark O$_3$ + 2-methyl-2-butene reactions, respectively. The aerosol loadings prior to beginning the irradiations and with all of the reactants present in the chamber were ≤ 0.6 μg m^{-3} in the experiments with 1,4-thioxane and 1,3,5-trimethylbenzene, 5−20 μg m^{-3} in the experiments with 1,4-dithiane, and 42 μg m^{-3} in the experiment with 1,4-dithiane + 1,3,5-trimethylbenzene.

In the two experiments in which OH radicals were generated from the photolysis of CH$_3$ONO in the presence of NO$_x$, the SMPS data showed that new particle formation occurred during the first irradiation period, with the increase in aerosol mass during the second and third irradiation periods being due to the growth of existing particles. As generally observed,[24] the aerosol yield, defined as {(aerosol formed, corrected for wall losses)/(organosulfur compound reacted)}, increased with the amount of aerosol present (or correspondingly, with the extent of reaction). Assuming that the aerosol had the same density as the organosulfur reactant, then the aerosol yields at the end of these reactions were 45% for both 1,4-thioxane and 1,4-dithiane. The aerosol yield during the last portion of the reaction (i.e., Δ(aerosol)/Δ(organosulfur compound) between the end of the second and third irradiation periods) were 60% for both 1,4-thioxane and 1,4-dithiane.

In the absence of NO$_x$, within the experimental uncertainties the aerosol yields were independent of the extent of reaction and were ~60% for both 1,4-thioxane and 1,4-dithiane (the same as during the last irradiation period in the experiments conducted in the presence of NO$_x$). Again, new particle formation occurred after the first addition of O$_3$; thereafter, aerosol mass increased through the growth of existing particles. Within the experimental uncertainties, the aerosol yield in the experiment with 1,4-thioxane + di-*n*-butyl ether was the same as for 1,4-thioxane alone. However, in the 1,4-dithiane + 1,3,5-trimethylbenzene experiment the aerosol formed was a factor of ~2 higher than expected if the aerosol yields from the experiments with 1,4-dithiane (60%) and 1,3,5-trimethylbenzene (7%) alone were additive, suggesting that in the presence of aerosol generated from 1,4-dithiane additional aerosol formation from 1,3,5-trimethylbenzene reaction products occurred. This observation is similar to aerosol formation from OH + divinyl sulfoxide + α-pinene mixtures compared to aerosol formation from OH + divinyl sulfoxide alone and OH + α-pinene alone.[25]

Clearly, aerosol formation from the reactions of OH radicals with 1,4-thioxane and 1,4-dithiane is significant, accounting for ~60% of the reaction products from both reactions, and essentially independent of the presence or absence of NO$_x$. It is possible that partitioning of 1,4-thioxane and 1,4-dithiane to the aerosol formed occurred to some extent, being more important at greater extents of reaction and more important in the experiments conducted in the absence of NO$_x$, and this could have been responsible at least in part for the observed curvature of the plots of eq 1 for the OH radical reactions.

Discussion

The rate constants measured here at room temperature for the reactions of OH radicals, NO$_3$ radicals, and O$_3$ with 1,4-thioxane and 1,4-dithiane are listed in Table 6 together with literature data for dimethyl sulfide,[12] diethyl sulfide,[5,10,11] tetrahydrothiophene,[4,13,26] diethyl ether,[1,27,28] and 1,4-dioxane.[29] The data for diethyl sulfide and diethyl ether are particularly relevant since the CH$_3$ groups in these compounds appear to be relatively unreactive,[30] and hence to a first approximation, 1,4-thioxane can be viewed as being composed of diethyl sulfide plus diethyl ether, while 1,4-dithiane can be viewed as two molecules of diethyl sulfide. Moreover, 1,4-dioxane, 1,4-thioxane, and 1,4-dithiane form a series in which the two O-atoms in 1,4-dioxane are progressively replaced by S-atoms. Consistent with dimethyl sulfide,[12] diethyl sulfide,[11] and alkyl ethers,[1] 1,4-thioxane and 1,4-dithiane are of low reactivity toward O$_3$. Under our experimental conditions, the measurements of rate constants for the reactions of 1,4-thioxane and 1,4-dithiane with OH radicals and NO$_3$ radicals were prone to complications from secondary reactions, and this was particularly evident for the OH radical reactions in the presence of NO$_x$. Literature studies show that for dimethyl sulfide, methyl ethyl sulfide, and diethyl sulfide, the OH radical reactions proceed by two independent pathways:[3,6−10,12]

$$\mathrm{OH + RCH_2SCH_2R' \rightarrow H_2O + RC^{\bullet}HSCH_2R'} \qquad (1a)$$

$$\mathrm{OH + RCH_2SCH_2R' \rightarrow RCH_2S(OH)CH_2R'} \qquad (1b)$$

with the OH-adduct RCH$_2$S(OH)CH$_2$R′ decomposing back to reactants in competition with reaction with O$_2$.

$$\mathrm{RCH_2S(OH)CH_2R' \rightarrow OH + RCH_2SCH_2R'} \qquad (7)$$

$$\mathrm{RCH_2S(OH)CH_2R' + O_2 \rightarrow products} \qquad (8)$$

In the absence of O$_2$, the measured rate constant is that for the H-atom abstraction pathway 1a, with the measured rate constant increasing with increasing O$_2$ concentration due to reaction 1b.[6−10,12] At high enough O$_2$ concentration, $k_8[\mathrm{O_2}] \gg k_7$ and the measured rate constant becomes $k_{1a} + k_{1b} = k_{\mathrm{abstr}} + k_{\mathrm{add}}$.[10,12] Note that for dimethyl sulfide and diethyl sulfide, reactions 1b and 7 are in the falloff regime at atmospheric pressure and below.[8−10] The values of k_{abstr}, k_{add}, and the measured rate constants for dimethyl sulfide[12] and diethyl sulfide[10] in 1 atm of air are given in Table 6.

TABLE 6: Room Temperature Rate Constants for the Reactions of OH and NO_3 Radicals and O_3 with 1,4-Dioxane, 1,4-Thioxane, 1,4-Dithiane, Dimethyl Sulfide, Diethyl Sulfide, Tetrahydrothiophene, and Diethyl Ether at Atmospheric Pressure of Air

	rate constant (cm^3 $molecule^{-1}$ s^{-1}) for reaction with		
reactant	OH	NO_3	O_3
1,4-dioxane	1.1×10^{-11}[a]		
1,4-thioxane[b]	2.0×10^{-11}	5.1×10^{-14}	$<2 \times 10^{-19}$
1,4-dithiane[b]	2.9×10^{-11}	5.9×10^{-14}	$<2.5 \times 10^{-19}$
dimethyl sulfide[c]	7.0×10^{-12} (air)	1.1×10^{-12}	$<2 \times 10^{-19}$
	$k_{abst} = 4.8 \times 10^{-12}$ $k_{add} \sim 4 \times 10^{-11}$		
diethyl sulfide	2.4×10^{-11} (air)[d]	4.8×10^{-12}[e]	2.8×10^{-19}[f]
	$k_{abstr} = 1.7 \times 10^{-11}$[d] $k_{add} = 2.6 \times 10^{-11}$[d]		
tetrahydrothiophene	2.0×10^{-11}[g]	4.1×10^{-12}[h]	
diethyl ether	1.3×10^{-11}[i]	3.1×10^{-15}[j]	$<1 \times 10^{-20}$[k]

[a] From Moriarty et al.[29] [b] This work. [c] From the IUPAC evaluation.[12] [d] From Williams et al.[10] [e] From Daykin and Wine.[5] [f] From Du et al.[11] [g] From Wine and Thompson[13] and Martin et al.[4] (in the absence of O_2). [h] From Cabañas et al.[26] [i] From Atkinson.[27] [j] From Chew et al.[28] [k] Estimated.[1]

In the presence of NO_x, our experiments showed a decrease in the measured rate constants for 1,4-thioxane and 1,4-dithiane with increasing O_2 concentration, and this is attributed, at least in part, to the occurrence of secondary reactions (as observed in OH + dimethyl sulfide in the presence of NO_x,[20−22] and further evident by the effect of added dimethyl sulfide on the measured rate constants). In the absence of NO_x, our data at 296 ± 2 K show no effect of varying the O_2 concentration by a factor of ~3.7 on the measured rate constants for 1,4-thioxane or 1,4-dithiane. This is in contrast to the case for dimethyl sulfide and diethyl sulfide, where the measured rate constants (from both absolute and relative rate studies in the case of dimethyl sulfide) increase with increasing O_2 concentration.[7−10,12]

Our measured rate constants for the reactions of NO_3 radicals with 1,4-thioxane and 1,4-dithiane are both similar and are factors of ~20, ~90, and ~75 lower than those for dimethyl sulfide,[12] diethyl sulfide,[5] and tetrahydrothiophene,[26] respectively, but an order of magnitude higher than that for diethyl ether.[28] Since the reactions of NO_3 radicals with dimethyl and diethyl sulfide proceed by initial NO_3 radical addition to the S-atom (with the rate-determining step being subsequent breakage of a C−H bond),[5,12] this suggests that the S-atom(s) in 1,4-thioxane and 1,4-dithiane are much less reactive than those in the alkyl sulfides toward NO_3 radical addition. The NO_3 radical reactions with 1,4-thioxane and 1,4-dithiane may therefore proceed mainly by H-atom abstraction from the C−H bonds of the CH_2 groups.

Our observed lack of evidence for an increasing rate constant for the OH radical reactions with 1,4-thioxane and 1,4-dithiane with increasing O_2 concentration in the absence of NO_x, and the fact that our room temperature rate constants are of a similar magnitude to those for H-atom abstraction from diethyl ether and diethyl sulfide, implies that the OH radical reactions proceed by H-atom abstraction from the C−H bonds of the CH_2 groups. Indeed, if the rate constant for diethyl ether and the rate constant for H-atom abstraction from diethyl sulfide are assumed to be almost totally due to H-atom abstraction from the CH_2 groups in each molecule, then the estimated rate constants for 1,4-thioxane and 1,4-dithiane are 3.0×10^{-11} cm^3 $molecule^{-1}$ s^{-1} and 3.4×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, respectively, reasonably similar to our measured values of 2.0×10^{-11} cm^3 $molecule^{-1}$ s^{-1} and 3.0×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, respectively. Furthermore, the room temperature rate constants for the OH radical reactions increase monotonically along the series 1,4-dioxane, 1,4-thioxane, and 1,4-dithiane (Table 6). Rate constants for the reaction of OH radicals with tetrahydrothiophene, of (1.97 ± 0.30) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 298 K[13] and (2.12 ± 0.16) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 293 K,[4] were measured in the absence of O_2 and presumably refer to H-atom abstraction. The rate constant for tetrahydrothiophene[4,13] is similar to that for H-atom abstraction from diethyl sulfide[10] and is consistent with our room temperature rate constants for 1,4-thioxane and 1,4-dithiane, if the latter are for H-atom abstraction. However, the Arrhenius activation energies derived here for the reactions of OH radicals with 1,4-thioxane and 1,4-dithiane ($E/R = -620$ K) are significantly more negative than those for H-atom abstraction by OH radicals from dimethyl sulfide ($E/R = 250$ K),[12] diethyl sulfide ($E/R \sim 0$ K),[10] tetrahydrothiophene ($E/R = -166 \pm 97$ K),[13] diethyl ether ($E/R \sim -200$ K over the temperature range studied here),[27] and, to a lesser extent, 1,4-dioxane (−332 ± 109 K).[29]

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