# Kinetics of the gas-phase reactions of NO<sub>3</sub> radicals with a series of alcohols, glycol ethers, ethers and chloroalkenes

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Using a relative rate method, rate constants have been measured for the gas-phase reactions of the NO<sub>3</sub> radical with methacrolein, a series of ethers, glycol ethers, alcohols and chloroalkenes at  $298 \pm 2$  K and atmospheric pressure of air. The rate constants determined (in units of  $10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) were: methacrolein,  $33 \pm 10$ ; diethyl ether,  $31 \pm 10$ ; di-*n*-propyl ether,  $49 \pm 16$ ; diisopropyl ether,  $40 \pm 13$ ; ethyl *tert*-butyl ether,  $45 \pm 14$ ; 1-methoxypropan-2-ol,  $\leq 15 \pm 5$ ; 2-butoxyethanol,  $\leq 31 \pm 11$ ; propan-1-ol,  $\leq 21 \pm 8$ ; propan-2-ol,  $\leq 17 \pm 6$ ; butan-1-ol,  $\leq 27 \pm 10$ ; butan-2-ol,  $\leq 25 \pm 8$ ; heptan-4-ol,  $\leq 60 \pm 20$ ; *cis*-1,2-dichloroethene,  $1.3 \pm 1.3$ ; 1,1-dichloroethene,  $18^{+9}_{-6}$ ; trichloroethene,  $3.6^{+2.0}_{-1.5}$ ; tetrachloroethene, <1.8; and 3chloropropene,  $5.8^{+3.0}_{-2.0}$ . Carbonyl products of the alcohol reactions arising after H-atom abstraction at the carbon atom to which the —OH group is attached were observed, and rate constants for this reaction pathway obtained. Significant discrepancies with the literature concern propan-2-ol, ethyl *tert*-butyl ether and 3-chloropropene, with our relative rate constants for these compounds being factors of *ca. 2, ca. 2, and ca. 8* lower, respectively, than previously reported absolute rate constant determinations.

Nitrate (NO<sub>3</sub>) radicals are an important reactive species present at concentrations up to  $ca. 1 \times 10^{10}$  molecule cm<sup>-3</sup> during night-time in the lower troposphere over continental areas.<sup>1,2</sup> In addition to daytime photolysis and reaction with the hydroxy (OH) radical and reaction with  $O_3$ , night-time reaction with the NO<sub>3</sub> radical is a potential chemical loss process for volatile organic compounds (VOCs) in the troposphere.<sup>3–7</sup> The relative importance of night-time reaction with the NO<sub>3</sub> radical versus daytime reaction with the OH radical depends on the NO3 and OH radical concentrations and on the rate constant ratio  $k_{NO_3}/k_{OH}$  (where  $k_{NO_3}$  and  $k_{OH}$  are the rate constants for the NO<sub>3</sub> and OH radical reactions, respectively). While reaction with the NO3 radical is most important for alkenes and other VOCs containing C=Cbond(s),<sup>4,6,7</sup> the literature rate constant ratios  $k_{NO3}/k_{OH}$  for ali-phatic aldehydes<sup>4,8</sup> and for certain alcohols,<sup>9</sup> ethers<sup>10,11</sup> and haloalkenes<sup>12-15</sup> are sufficiently high that night-time NO<sub>3</sub> radical reactions with these VOCs could be significant. Of particular interest is the observation that the room temperature rate constants for the reactions of the NO<sub>3</sub> radical with ethanol, propan-2-ol, and ethers containing  $-CH_2$ -and  $\geq CH$ - groups are in the  $10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> range,9-11 some two orders of magnitude higher than the room temperature rate constants for the corresponding alkanes.4,5,

To date, there have been only few kinetic studies of the gasphase reactions of the NO<sub>3</sub> radical with  $\ge C_2$  alcohols and ethers,<sup>9-11,16,17</sup> and for the  $\ge C_2$  alcohols only for ethanol and propan-2-ol have rate constants been measured.<sup>9,16</sup> While the kinetics of the reactions of the NO<sub>3</sub> radical with chloroethenes have been studied by several research groups with generally good agreement,<sup>4,18–22</sup> a discrepancy of a factor of *ca*. 10 in the room temperature rate constant for 3chloropropene (allyl chloride) exists between the relative rate study of Atkinson and co-workers<sup>4,18</sup> and the absolute rate study of Martinez *et al.*<sup>15</sup>

In this work, we have used a relative rate method to measure the room temperature rate constants for the gasphase reactions of the NO<sub>3</sub> radical with a series of alcohols and ethers, and observed the carbonyl products formed from the alcohol reactions. We have re-studied the reactions of the radical with NO<sub>2</sub> 1-methoxypropan-2-ol and 2butoxyethanol.<sup>23</sup> because the rate constants for these glycol ethers are lower than expected on the basis of the alcohol and ether literature data and structure-reactivity considerations.<sup>23</sup> Finally, because of the above noted order of magnitude discrepancy between the relative rate<sup>4,18</sup> and absolute rate  $constant^{15}$  determinations for 3-chloropropene, we have remeasured the NO<sub>3</sub> radical reactions with a series of chloroethenes and with 3-chloropropene.

# **Experimental**

Experiments were carried out in the dark in *ca.* 7500 l Teflon chambers at 298  $\pm$  2 K and 740 Torr total pressure of purified air at *ca.* 5% humidity. The chambers are equipped with a Teflon-coated fan to ensure rapid mixing of reactants during their introduction into the chamber. NO<sub>3</sub> radical reaction rate constants were determined using a relative rate method in which the relative rates of disappearance of the organic and a reference compound, whose NO<sub>3</sub> radical reaction rate constant is reliably known, were measured in the presence of NO<sub>3</sub> radicals.<sup>24,25</sup> Providing that the organic and the reference compound react only with NO<sub>3</sub> radicals, then

$$\ln\left(\frac{[\operatorname{organic}]_{t_0}}{[\operatorname{organic}]_t}\right) - D_t = \frac{k_1}{k_2} \left\{ \ln\left(\frac{[\operatorname{reference\ compound}]_{t_0}}{[\operatorname{reference\ compound}]_t}\right) - D_t \right\}$$
(I)

where  $[\text{organic}]_{t_0}$  and  $[\text{reference compound}]_{t_0}$  are the concentrations of the organic and the reference compound, respectively, at time  $t_0$ , and  $[\text{organic}]_t$  and  $[\text{reference compound}]_t$  are the corresponding concentrations at time t,  $D_t$  is a term to take into account dilution due to additions to the chamber during an experiment, and  $k_1$  and  $k_2$  are the rate constants for

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$$NO_3 + organic \rightarrow products$$
 (1)

$$NO_3$$
 + reference compound  $\rightarrow$  products (2)

Plots of  $\{\ln([\operatorname{organic}]_{t_0}/[\operatorname{organic}]_t) - D_t\}$  against  $\{\ln([\operatorname{reference compound}]_{t_0}/[\operatorname{reference compound}]_t) - D_t\}$  should therefore be straight lines with zero intercept and slopes of  $k_1/k_2$ .

 $NO_3$  radicals were generated from the thermal decomposition of  $N_2O_5,{}^{24}$ 

$$N_2O_5 \rightarrow NO_3 + NO_2 \tag{3}$$

and the initial reactant concentrations (in molecule  $cm^{-3}$ units) were: alcohol, glycol ether, ether or chloroalkene, ca.  $2.4 \times 10^{13}$ ; reference compound(s), ca. (2.4-4.8) × 10^{13}; and  $NO_2$ ,  $(0-2.4) \times 10^{14}$ . When  $NO_2$  was not initially present,  $2.0 \times 10^{16}$  molecule cm<sup>-3</sup> of ethane was added to the chamber to scavenge any OH radicals or (for the chloroalkenes) Cl atoms formed during the reactions.18,25 Typically, three additions of N<sub>2</sub>O<sub>5</sub> were made to the chamber during an experiment, with each addition of N<sub>2</sub>O<sub>5</sub> corresponding to an initial concentration of N<sub>2</sub>O<sub>5</sub> in the chamber of  $(5-15) \times 10^{13}$  molecule cm<sup>-3</sup>. The value of  $D_t$  was 0.0012 or 0.0028 per  $N_2O_5$  addition, depending on the chamber used. The reference compound for the experiments with the alcohols, glycol ethers, and ethers (apart from ethyl tert-butyl ether which co-eluted with methacrolein; see below) was methacrolein, chosen because its rate constant for reaction with the  $NO_3$  radical<sup>26</sup> is within the range of the literature rate constants for the glycol ethers, alcohols, and ethers studied here<sup>9-11,23</sup> and because it could be analyzed using the same sampling and analysis procedures as the alcohols, glycol ethers, and ethers. 2,3-Dimethylbutane was used as the reference compound for the experiments with the chloroalkenes, for similar reasons.<sup>4</sup> Experiments were also carried out to measure the rate constant for the NO<sub>3</sub> radical reaction with methacrolein using propene and but-1-ene as the reference compounds, and one experiment was carried out for 3chloropropene using propene as the reference compound.

The concentrations of the organic and reference compounds were measured by gas chromatography with flame ionization detection (GC-FID). For analysis of the reference compounds propene, but-1-ene and 2,3-dimethylbutane, and of the chloroalkenes, gas samples were collected in 100 cm<sup>3</sup> all-glass, gastight syringes and introduced via a 1 cm<sup>3</sup> stainless steel loop and gas sampling valve onto a 30 m DB-5 megabore column, initially held at -25 °C and then temperature programmed to 200 °C at 8 °C min<sup>-1</sup>. For the analysis of methacrolein, 1methoxypropan-2-ol, 2-butoxyethanol, propan-1- and -2-ol, butan-1- and -2-ol, heptan-4-ol, diethyl ether, di-n-propyl ether, diisopropyl ether, ethyl tert-butyl ether and (for the experiment with propene as the reference compound) 3chloropropene, 100 cm<sup>3</sup> gas samples were collected from the chamber onto Tenax-TA solid adsorbent, with subsequent thermal desorption at ca. 225 °C onto a 30 m DB-1701 megabore column held at -40 °C and then temperature programmed to 200 °C at 8 °C min<sup>-1</sup>.

The sources of the chemicals used and their stated purities were: acetone (HPLC grade), Fisher Scientific; butanal (99%), butan-2-ol (99.5%), butan-2-one (99+%), 2-butoxyethanol (99+%), 3-chloropropene (99%), *cis*-dichloroethene (97%), 1,1-dichloroethene (99%), diethyl ether (99.9%), diisopropyl ether (99%), di-*n*-propyl ether (99+%), 2,3-dimethylbutane (99%), ethyl *tert*-butyl ether (99%), heptan-4-ol (98%), heptan-4-one (98%), methacrolein (95%), methoxyacetone (97%), 1methoxypropan-2-ol (98%), propanal (99+%), tetrachloroethene (99.9+%) and trichloroethene (99.5+%), Aldrich Chemical Company; butan-1-ol, propan-1-ol and propan-2-ol, Mallinckrodt; and propene ( $\geq$ 99.0% and  $\geq$  99.6%) and but-1-ene ( $\geq$  99.0%), Matheson Gas Products. N<sub>2</sub>O<sub>5</sub> was prepared and stored as described previously,<sup>24</sup> and NO<sub>2</sub> was prepared as needed by reacting NO with an excess of O<sub>2</sub>.

# **Results and Discussion**

#### Rate constants for methacrolein

A series of experiments were carried out to measure the rate constant for the reaction of the NO<sub>3</sub> radical with methacrolein relative to those for propene and but-1-ene. The data obtained are plotted in accordance with eqn. (I) in Fig. 1, and the rate constant ratios  $k_1/k_2$  obtained by linear least-squares analyses of these data are given in Table 1. No effect of the initial NO<sub>2</sub> concentration, over the range (0–9.6) × 10<sup>13</sup> molecule cm<sup>-3</sup>, on the rate constant ratios  $k_1/k_2$  was observed.

#### Rate constants for ethers

Rate constants for the reactions of the  $NO_3$  radical with diethyl ether, di-*n*-propyl ether and diisopropyl ether were



Fig. 1 Plots of eqn. (I) for the gas-phase reactions of the  $NO_3$  radical with methacrolein, with propene and but-1-ene as the reference compounds. The data for methacrolein with propene as the reference compound have been displaced vertically by 0.4 units for clarity.

**Table 1** Rate constant ratios  $k_1/k_2$  for the gas-phase reactions of the NO<sub>3</sub> radical at 298 ± 2 K and 740 Torr of air

organic	reference compound	$k_{1}/k_{2}^{a}$
methacrolein	propene	$0.324 \pm 0.017$
methacrolein	but-1-ene	$0.259 \pm 0.011$
but-1-ene	propene	$1.25 \pm 0.09$
diethyl ether	methacrolein	$0.929 \pm 0.048$
di-n-propyl ether	methacrolein	1.49 ± 0.11
diisopropyl ether	methacrolein	$1.22 \pm 0.07$
di-n-propyl ether	diethyl ether	$1.64 \pm 0.04$
ethyl tert-butyl ether	diethyl ether	$1.46 \pm 0.05$
cis-1,2-dichloroethene	2,3-dimethylbutane	$0.29 \pm 0.26$
1,1-dichloroethene	2,3-dimethylbutane	$4.07 \pm 0.34$
trichloroethene	2,3-dimethylbutane	$0.82 \pm 0.21$
tetrachloroethene	2,3-dimethylbutane	$0.21 \pm 0.18$
3-chloropropene	2,3-dimethylbutane	$1.31 \pm 0.11$
3-chloropropene	propene	$0.073 \pm 0.025$

<sup>a</sup> Indicated errors are two least-squares standard deviations.



Fig. 2 Plots of eqn. (I) for the gas-phase reactions of the  $NO_3$  radical with diethyl ether, diisopropyl ether and di-*n*-propyl ether, with methacrolein as the reference compound. The data for diisopropyl ether and di-*n*-propyl ether have been displaced vertically by 0.2 and 0.4 units, respectively, for clarity.

measured relative to methacrolein, and the data obtained are plotted in accordance with eqn. (I) in Fig. 2. For ethyl tertbutyl ether, which co-eluted with methacrolein on the DB-1701 column, a rate constant was obtained relative to that for diethyl ether in reacting NO<sub>3</sub>-N<sub>2</sub>O<sub>5</sub>-NO<sub>2</sub>-diethyl etherethyl tert-butyl ether-di-n-propyl ether-air mixtures (di-npropyl ether was included to check the consistency of the data), and the data are shown in Fig. 3. The rate constant ratios  $k_1/k_2$  for these experiments involving ethers are also given in Table 1, and the rate constant ratio  $k_1$ (di-*n*-propyl ether)/ $k_2$ (methacrolein) = 1.49  $\pm$  0.11 measured directly is in excellent agreement with the value of  $1.52 \pm 0.09$  calculated the separate measurements of  $k_1$ (di-*n*-propyl from ether)/ $k_2$ (diethyl ether) and  $k_1$ (diethyl ether)/ $k_2$ (methacrolein). Analogous to the reactions of the NO<sub>3</sub> radical with propene and methacrolein, no effect of the initial NO2 concentration on the rate constant ratios  $k_1/k_2$  was observed over the range  $(0-4.8) \times 10^{13}$  molecule cm<sup>-3</sup>.

## Rate constants for glycol ethers and alcohols

In contrast with the data shown in Fig. 1-3 for methacrolein and the four ethers studied, for the two glycol ethers and the



Fig. 3 Plots of eqn. (I) for the gas-phase reactions of the  $NO_3$  radical with ethyl *tert*-butyl ether and di-*n*-propyl ether, with diethyl ether as the reference compound. The data for di-*n*-propyl ether have been displaced vertically by 0.2 units for clarity.

alcohols studied five the rate constant ratios  $k_1/k_2$  (methacrolein) showed a dependence on the initial NO<sub>2</sub> concentration. The measured rate constant ratios were invariant of the initial  $NO_2$  concentration over the range (0- $(4.8) \times 10^{13}$  molecule cm<sup>-3</sup>, but increased at higher initial  $NO_2$  concentrations of  $9.6 \times 10^{13}$  molecule cm<sup>-3</sup> and  $2.4 \times 10^{14}$  molecule cm<sup>-3</sup> [for heptan-4-ol, data were obtained only for initial NO2 concentrations in the range (0-4.8)  $\times$  10<sup>13</sup> molecule cm<sup>-3</sup>]. Typical of the data obtained, rate constant ratios as a function of the initial NO<sub>2</sub> concentration are given in Table 2 for the reactions involving propan-2-ol and butan-2-ol, and the experimental data obtained for propan-2-ol, butan-2-ol and heptan-4-ol at initial NO2 concentrations in the range  $(0-4.8) \times 10^{13}$  molecule cm<sup>-3</sup> are plotted in accordance with eqn. (I) in Fig. 4. Rate constant ratios  $k_1/k_2$  obtained at initial NO<sub>2</sub> concentrations of (0–4.8) × 10<sup>13</sup> molecule cm<sup>-3</sup> are given in Table 3 for the glycol ethers and alcohols studied.

GC-FID analyses showed the formation of acetone from propan-2-ol, butan-2-one from butan-2-ol, heptan-4-one from heptan-4-ol, propanal from propan-1-ol, butanal from butan-1-ol, and methoxyacetone from 1-methoxypropan-2-ol. These products are expected to arise after abstraction of an H-atom

**Table 2** Rate constant ratios  $k_1/k_2$  (methacrolein) and carbonyl formation yields for the reactions of the NO<sub>3</sub> radical with propan-2-ol and butan-2-ol as a function of the initial NO<sub>2</sub> concentration

$[NO_2]/$ 10 <sup>13</sup> molecule cm <sup>-3</sup>	$k_1/k_2$ (methacrolein) <sup>a</sup>	product yield <sup>a</sup>	$\frac{k_1 \times \text{product yield}^a}{k_2 \text{(methacrolein)}}$
propan-2-ol <sup>b</sup>			
0	$0.556 \pm 0.060$	$0.779 \pm 0.062$	$0.444 \pm 0.060$
2.4	$0.486 \pm 0.036$	$0.794 \pm 0.048$	$0.386 \pm 0.037$
2.4	$0.551 \pm 0.088$	$0.716 \pm 0.087$	$0.395 \pm 0.080$
4.8	$0.587 \pm 0.022$	$0.669 \pm 0.046$	$0.393 \pm 0.031$
9.6	$0.757 \pm 0.085$	$0.566 \pm 0.031$	$0.428 \pm 0.054$
24	$1.13 \pm 0.18$	$0.390 \pm 0.045$	$0.441 \pm 0.087$
butan-2-ol <sup>c</sup>			
0	$0.809 \pm 0.057$	$0.798 \pm 0.026$	$0.646 \pm 0.051$
2.4	$0.722 \pm 0.045$	$0.802 \pm 0.037$	$0.579 \pm 0.045$
2.4	$0.786 \pm 0.082$	$0.732 \pm 0.045$	$0.575 \pm 0.070$
4.8	$0.837 \pm 0.026$	$0.706 \pm 0.078$	$0.591 \pm 0.068$
9.6	$1.05 \pm 0.11$	$0.611 \pm 0.109$	$0.642 \pm 0.133$
24	$1.35 \pm 0.15$	$0.473 \pm 0.103$	$0.639 \pm 0.147$

<sup>a</sup> Indicated errors are two least-squares standard deviations. <sup>b</sup> Product is acetone. <sup>c</sup> Product is butan-2-one.



Fig. 4 Plots of eqn. (I) for the gas-phase reactions of the NO<sub>3</sub> radical with propan-2-ol, butan-2-ol and heptan-4-ol, with methacrolein as the reference compound, at initial NO<sub>2</sub> concentrations of  $(0-4.8) \times 10^{13}$  molecule cm<sup>-3</sup>. The data for butan-2-ol and heptan-4-ol have been displaced vertically by 0.2 units for clarity.

from the same carbon atom as the -OH groups,<sup>5</sup> as shown, for example, for propan-2-ol in Scheme 1.

The measured formation yields of these products, defined as ([carbonyl] measured)/([alcohol] reacted) were essentially independent of the initial NO<sub>2</sub> concentration for NO<sub>2</sub> concentrations in the range  $(0-4.8) \times 10^{13}$  molecule cm<sup>-3</sup>, but decreased at higher initial NO<sub>2</sub> concentrations of  $9.6 \times 10^{13}$  molecule cm<sup>-3</sup> and  $2.4 \times 10^{14}$  molecule cm<sup>-3</sup>. Representative of the data obtained for propan-2-ol, butan-2-ol and 1-methoxypropan-2-ol, the acetone and butan-2-one formation yields from propan-2-ol and butan-2-ol, respectively, are given as a function of the initial NO<sub>2</sub> concentrations in Table 2. The average carbonyl formation yields from the reactions of the NO<sub>3</sub> radical with 1-methoxypropan-2-ol and the alcohols studied, obtained from experiments with initial NO<sub>2</sub> concentrations of  $(0-4.8) \times 10^{13}$  molecule cm<sup>-3</sup>, are given in Table 3.

The measured upper limit to the room temperature rate constant for the reaction of the NO<sub>3</sub> radical with acetone<sup>27</sup> is two orders of magnitude lower than the measured rate constant for propan-2-ol,<sup>9</sup> and butan-2-one and heptan-4-one formed from butan-2-ol and heptan-4-ol, respectively, are also

	$CH_3C(O)CH_3 + 1$	HO <sub>2</sub>
	O <sub>2</sub>	
	→ HNO <sub>3</sub> + CH <sub>3</sub> Ċ(OH)CH <sub>3</sub>	(1b)
NO $+$ CH.CH(OH)CH. —	$\rightarrow$ HNO <sub>3</sub> + CH <sub>3</sub> CH(OH)ĊH <sub>2</sub>	(1a)



Fig. 5 Plots of eqn. (I) for the gas-phase reactions of the  $NO_3$  radical with 3-chloropropene and 1,1-dichloroethene, with 2,3-dimethylbutane as the reference compound

expected to be much less reactive than the precursor alcohol, and the same may be the case for methoxyacetone formed from 1-methoxypropan-2-ol. Hence, secondary reactions of the NO<sub>3</sub> radical with the ketone products of these secondary alcohols and 1-methoxypropan-2-ol were of no importance. However, aldehydes are much more reactive towards the NO<sub>3</sub> radical,4,8 and the secondary reactions of propanal and butanal need to be considered in deriving their formation yields from the NO<sub>3</sub> radical reactions with propan-1-ol and butan-1-ol. The rate constants for the reactions of the NO<sub>3</sub> radical with propanal and butanal have recently been measured,<sup>8</sup> and are  $5.7 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $1.09 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively, at 298 ± 2 K.<sup>8</sup> With rate constants of this magnitude, the propanal and butanal formation yields, corrected for secondary reactions with the NO<sub>3</sub> radical, from propan-1-ol and butan-1-ol, respectively, are estimated to be close to unity.

#### Rate constants for chloroalkenes

2,3-Dimethylbutane was used as the reference compound for the chloroalkenes studied [*cis*-1,2-dichloroethene, 1,1dichloroethene, trichloroethene, tetrachloroethene and 3chloropropene (allyl chloride)], with an additional experiment being carried out for 3-chloropropene with propene as the reference compound. For these experiments, sufficient ethane was included in the reactant mixtures to scavenge >98% of any Cl atoms and >80% of any OH radicals formed during these NO<sub>3</sub> radical reactions. Because of the low reactivity of 2,3-dimethylbutane and most of the chloroalkenes towards the NO<sub>3</sub> radical,<sup>4</sup> the fractions of 2,3-dimethylbutane and the

**Table 3** Rate constant ratios  $k_1/k_2$  (methacrolein) and product formation yields for the gas-phase reactions of the NO<sub>3</sub> radical with alcohols and glycol ethers at 298 ± 2 K from experiments with initial NO<sub>2</sub> concentrations in the range (0–4.8) × 10<sup>13</sup> molecule cm<sup>-3</sup>

organic	$k_1/k_2$ (methacrolein) <sup>a</sup>	product	product yield <sup>a</sup>
propan-2-ol butan-2-ol heptan-4-ol propan-1-ol butan-1-ol 1-methoxypropan-2-ol 2-butoxyethanol	$\begin{array}{c} 0.519 \pm 0.053 \\ 0.754 \pm 0.065 \\ 1.81 \pm 0.25 \\ 0.65 \pm 0.12 \\ 0.81 \pm 0.16 \\ 0.452 \pm 0.049 \\ 0.95 \pm 0.16 \end{array}$	acetone butan-2-one heptan-4-one propanal butanal methoxyacetone	$\begin{array}{c} 0.76 \pm 0.09 \\ 0.79 \pm 0.07 \\ 0.75 \pm 0.12 \\ > 0.55 \pm 0.07^{b} \\ > 0.22 \pm 0.04^{b} \\ 0.52 \pm 0.08 \end{array}$

<sup>*a*</sup> Indicated errors are two least-squares standard deviations. <sup>*b*</sup> Calculated formation yield depends on the rate constant for the reaction of the NO<sub>3</sub> radical with the aldehyde product (see text). The lower limit cited is with no correction being made for secondary reactions of the aldehyde product with the NO<sub>3</sub> radical.

chloroalkenes reacted during these NO<sub>3</sub> radical reactions were fairly low (typically up to 20-25% for 2,3-dimethylbutane and <20% for *cis*-1,2-dichloroethene, trichloroethene and tetrachloroethene). Combined with an appreciable amount of scatter in the GC analyses of cis-1,2-dichloroethene, trichloroethene and tetrachloroethene, significant uncertainties in the rate constant ratios  $k_1/k_2$  for these three chloroethenes were observed (Table 1), and the data for these three chloroethenes are of only semi-quantitative use. However, the chromatography was significantly more precise for the two more reactive chloroalkenes 1,1-dichloroethene and 3-chloropropene, and the rate constant ratios  $k_1/k_2$  for these reactants had relatively low uncertainties (Table 1). The experimental data obtained for 1,1-dichloroethene and 3chloropropene are plotted in accordance with eqn. (I) in Fig. 5. For the experiment using propene as the reference compound, analyses of 3-chloropropene were carried out using both the loop injection/DB-5 column system and the thermal desorption/DB-1701 column system, with good agreement between these analyses.

## Discussion

## Rate constant for methacrolein

The measured rate constant ratios  $k_1/k_2$  for the reaction of the NO<sub>3</sub> radical with methacrolein relative to those for propene and but-1-ene are placed on an absolute basis by use of recommended rate constants for the reaction of the NO<sub>3</sub> radical with propene and but-1-ene at 298 K of  $9.49 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> ( $\pm 35\%$ )<sup>5,7</sup> and  $1.35 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> ( $\pm 30\%$ ),<sup>7</sup> respectively, and the rate constants  $k_1$ (methacrolein) are given in Table 4 together with literature values. Using these recommended rate constants  $k_2$ , our rate constants for methacrolein relative to propene and but-1-ene agree to within 14% (Table 4). The average of these values is consistent with the upper limit determined by Rudich et al.,<sup>28</sup> but is ca. 25% lower than our previous measurement<sup>26</sup> carried out relative to propene. Because the present kinetic study of methacrolein was much more extensive than our previous study,<sup>26</sup> the average of the rate constants measured here relative to those for propene and but-1-ene [(3.3  $\pm$  1.0)  $\times$  10<sup>-15</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298  $\pm$  2 K] is used to place the rate constant ratios obtained with methacrolein as a reference compound on an absolute basis.

Our present rate constant ratio k<sub>2</sub>(but-1ene)/ $k_2$ (propene) = 1.25 ± 0.09 at 298 ± 2 K, obtained from NO<sub>3</sub>-NO<sub>2</sub>-N<sub>2</sub>O<sub>5</sub>-methacrolein-propene-but-1reacting ene-air mixtures (Table 1), agrees with the literature room temperature rate constant ratios of Atkinson et al.<sup>24</sup>  $(1.304 \pm 0.012)$  and Barnes et al.<sup>29</sup>  $(1.34 \pm 0.20)$ , but is somewhat lower that the rate constant ratio derived from the literature recommendations for the reactions of the NO<sub>3</sub> radical with but-1-ene<sup>7</sup> and propene<sup>5,7</sup> at 298 K, of 1.42. This probably suggests that the rate constant for the reaction of the NO<sub>3</sub> radical with propene is 10-15% higher than presently recommended,<sup>5,7</sup> and further absolute rate constant studies of the reactions of the NO<sub>3</sub> radical with both propene and but-1ene are clearly warranted.

## Rate constants for ethers

The rate constants measured here for diethyl ether, di-*n*propyl ether, diisopropyl ether and ethyl *tert*-butyl ether are given in Table 4 together with the literature data of Langer and Ljungström.<sup>10,11</sup> Our relative rate constant for diethyl ether is in good or reasonable agreement with the absolute and relative rate constants, respectively, of Langer and Ljungström.<sup>10</sup> Although our rate constants for di-*n*-propyl ether and diisopropyl ether are slightly lower than the absolute and relative rate constants of Langer and Ljungström,<sup>10</sup> they agree within the overall uncertainties. However, our relative rate constant for ethyl *tert*-butyl ether is significantly lower, by a factor of *ca.* 2, than both the absolute and relative rate measurements of Langer and Ljungström,<sup>11</sup> for reasons which are not presently known. While the relative rate constants from this work as well as previous studies are uncertain to varying degrees (probably around  $\pm 30\%$ ) because of the significant uncertainties in the rate constants for the reactions of the NO<sub>3</sub> radical with the slowly reacting reference compounds used, this discrepancy of a factor of two is outside of the uncertainties associated with uncertainties in the rate constants  $k_2$  for most of the reference compounds used in this and the previous work<sup>11</sup> for ethyl *tert*-butyl ether.

## Reactions with alcohols and glycol ethers

Our kinetic and product data for alcohols show (see Table 2, for example) that (a) the measured rate constants increase with the increasing initial  $NO_2$  concentration, (b) the formation yields of the carbonyl products arising after abstraction of an H-atom from the carbon atom to which the -OH group is attached decrease with increasing initial NO2 concentration, and (c) that  $\{(\text{carbonyl yield}) \times (\text{measured rate constant})\}$  is invariant of the initial NO<sub>2</sub> concentration. These observations are consistent with the study of Langer and Ljungström<sup>9</sup> where they observed reaction of N2O5 with the alcohols studied leading to alkyl nitrate formation under similar conditions as used here (but with a smaller reaction vessel and higher reactant concentrations). It is possible that these  $N_2O_5$ reactions with the alcohols (and glycol ethers) are heterogeneous. Computer modeling calculations using the Acuchem program<sup>30</sup> showed that the average  $N_2O_5/NO_3$ concentration ratios in our reaction systems were 950, 1250, 1750, 3000 and 7100 for initial NO<sub>2</sub> concentrations of 0,  $2.4 \times 10^{13}$ ,  $4.8 \times 10^{13}$ ,  $9.6 \times 10^{13}$  and  $2.4 \times 10^{14}$  molecule  $cm^{-3}$ , respectively, during the first *ca*. 1.7 h after the first addition of N<sub>2</sub>O<sub>5</sub> to the chamber, with little change expected thereafter. Thus, the average  $N_2O_5/NO_3$  concentration ratio increases by less than a factor of 2 for initial NO<sub>2</sub> concentrations increasing from zero to  $4.8 \times 10^{13}$  molecule cm<sup>-3</sup>, but above  $4.8 \times 10^{13}$  molecule cm<sup>-3</sup> the average N<sub>2</sub>O<sub>5</sub>/NO<sub>3</sub> concentration ratio increases almost linearly with the initial NO<sub>2</sub> concentration.

The rate constants measured here at low initial NO<sub>2</sub> concentrations of  $(0-4.8) \times 10^{13}$  molecule cm<sup>-3</sup> may still include a contribution to the measured loss rates of the alcohols and glycol ethers from the N2O5 reactions, and hence the measured rate constants are strictly upper limits to the rate constants for the homogeneous gas-phase NO<sub>3</sub> radical reactions. The rate constants measured here for 1-methoxypropan-2-ol, 2-butoxyethanol, propan-1- and -2-ol, butan-1- and -2-ol and heptan-4-ol (cited as upper limits) are given in Table 4 together with the available literature data.<sup>9,16</sup> Our measured rate constants for 1-methoxypropan-2-ol and 2-butoxyethanol are in excellent agreement with our previous, less extensive measurements<sup>23</sup> (Table 4). For propan-2-ol, our measured rate constant is consistent with the upper limit obtained by Wallington et al.,<sup>16</sup> but is almost a factor of two lower than the absolute measurement of Langer and Ljungström.<sup>9</sup> The reasons for this discrepancy is presently not known.

The product {(measured rate constant)  $\times$  (carbonyl yield)} provides a rate constant for reaction (1b), involving abstraction of an H-atom from the carbon atom to which the -OH group is attached, as shown for example for propan-2ol in Scheme 1.

The measured rate constants  $k_1$  given in Table 4 can be combined with the measured carbonyl formation yields given in Table 3 to obtain rate constants  $k_{1b}$  (in units of  $10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) at 298 ± 2 K of: propan-2 ol, 13 ± 5; butan-2-ol, 20 ± 7; heptan-4-ol, 45 ± 17; and 1-methoxypropan-2ol, 7.8 ± 2.8. Because of uncertainties in deriving the propanal

Table 4	Room temperature rate constants $k_1$	for the	gas-phase	reactions	of the 1	$NO_3$	radical	with	organics
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	$k_1/10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$			
organic	this work <sup>a</sup>	literature <sup>b</sup>	$T/\mathrm{K}$	ref.
methacrolein	$30.7 \pm 10.9^{c}$	<80	298	28
	$35.0 \pm 10.6^{a}$ $33 \pm 10^{e}$	$44 \pm 17^{J}$	$296 \pm 2$	26
diethyl ether	$31 \pm 10$	$28.0\pm2.3$	295	10
di n propul other	$40 \pm 16$	$24.6^{g}$	295	10
di- <i>n</i> -propyr ether	$49 \pm 10$	$66.2^{h}$	295	10
diisopropyl ether	$40 \pm 13$	$51.8 \pm 9.8$	295	11
		$51.5^{i}$	295	11
ethyl <i>tert</i> -butyl ether	45 + 14	$48.3 \pm 17.0^{\circ}$ $87.1 \pm 22.6$	295	11
ethyl tert butyl ether		$99.4^{i}$	295	11
		$90.3 \pm 32.1^{f}$	295	11
1-methoxypropan-2-ol	$\leq 15 \pm 5$	$17 \pm 7^{f}$	$296 \pm 2$	23
2-butoxyethanol	$\leq 31 \pm 11$	$30 \pm 12^{f}$	$296 \pm 2$	23
propan-1-ol	$\leq 21 \pm 8$			
propan-2-ol	$\leq 17 \pm 6$	$31.3 \pm 6.4$	295	9
buton 1 ol	< 27 + 10	≤23	$298 \pm 2$	16
butan-2-ol	$\leq 27 \pm 10$ $< 25 \pm 8$			
hentan-4-ol	$\leq 25 \pm 6$ $\leq 60 \pm 20$			
cis-1,2-dichloroethene	1.3 + 1.3	$1.39 + 0.13^{j}$	298 + 2	18
···· -,- ······		$1.9 \pm 0.6^k$	$295 \pm 2$	20
		$2.13 \pm 0.34^{j}$	299	22
		$2.27 \pm 0.15^{i}$	299	22
1,1-dichloroethene	$18^{+9}_{-6}$	$12.3 \pm 1.5^{j}$	$298 \pm 2$	18
		$12.5 \pm 1.2^{k}$	$295 \pm 2$	20
		$12 \pm 3$	301	21
		$18.8 \pm 1.2$ 167 + 10 <i>i</i>	295	22
		$10.7 \pm 1.0^{\circ}$ 193 + 07 <sup>l</sup>	296	22
		$15.5 \pm 0.7$ $15.1 \pm 0.8^{g}$	299	22
trichloroethene	$3.6^{+2.0}_{-1.5}$	$2.81 \pm 0.17^{j}$	$\frac{2}{298} + 2$	18
		$2.7 \pm 0.6^{k}$	$295 \pm 2$	20
		$4.43 \pm 0.32$	295	22
		$3.67 \pm 0.37^{j}$	298	22
		$6.2 \pm 0.2^{l}$	298	22
tetrachloroethene	<1.8	< 0.52	$298 \pm 2$	18
		$0.96 \pm 0.81$	295	22
		$0.82 \pm 0.24^{\circ}$ 0.48 <sup>1</sup>	299 200	22
3-chloropropene	<b>5</b> 8+3.0	$535 \pm 021^{j}$	$\frac{233}{298} + 2$	18
e emeropropene	$6.9 \pm 3.4^{\circ}$	49 + 2	298 - 2	15

<sup>*a*</sup> At 298±2 K. Placed on an absolute basis by use of rate constants at 298 K of  $k_2$ (propene) = 9.49 × 10<sup>-15</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (±35%),<sup>5,7</sup>  $k_2$  (but-1-ene) = 1.35 × 10<sup>-14</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (±30%),<sup>7</sup>  $k_2$  (methacrolein) = 3.3 × 10<sup>-15</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (±30%) (this work) and  $k_2$ (2,3-dimethylbutane = 4.4 × 10<sup>-16</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (uncertain to a factor of 1.5).<sup>4,7</sup> Indicated uncertainties include the estimated overall uncertainties in the rate constants  $k_2$ . <sup>*b*</sup> Absolute rate studies, unless noted otherwise. <sup>*c*</sup> Relative to propene. <sup>*d*</sup> Relative to but-1-ene. <sup>*e*</sup> Average value. <sup>*f*</sup> Relative to  $k_2$ (propene) = 4.59 × 10<sup>-13</sup> exp(-1156/T) cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (±35%).<sup>5,7</sup> <sup>*g*</sup> Relative to  $k_2$ (acetaldehyde) = 1.44 × 10<sup>-12</sup> exp(-1862/T) cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1,4,5,6</sup> Relative to  $k_2$ (1-chlorobut-2-ene) = 2.1 × 10<sup>-14</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1,4,5,7</sup> k Relative to  $k_2$ (3-chlorobut-1-ene) = 2.8 × 10<sup>-15</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1,1,3,7</sup> Relative to  $k_2$ (ethene) = 4.88 × 10<sup>-18</sup> exp(-2282/T) cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1,4,5,7,7</sup> k Relative to an equilibrium constant for the N<sub>2</sub>O<sub>5</sub>  $\rightleftharpoons$  NO<sub>3</sub> + NO<sub>2</sub> reactions of 5.00 × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> at 295 K.<sup>4,1</sup> Relative to  $k_2$ (vinyl chloride) = 1.8 × 10<sup>-13</sup> exp(-1770/T) cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1,22</sup>

and butanal yields from the propan-1-ol and butan-1-ol reactions, respectively (because of the relatively high reactivities of propanal and butanal towards the NO<sub>3</sub> radical<sup>8</sup>), no meaningful estimates of the rate constants  $k_{1b}$  can be made for these two primary alcohols (although the values of  $k_{1b}$  must obviously be less than the measured upper limits to the rate constants  $k_1$  given in Table 4). For the secondary alcohols studied, the rate constant  $k_{1b}$  increases along the series propan-2-ol, butan-2-ol and heptan-4-ol. This is consistent with predictions of the estimation method proposed by Atkinson<sup>4</sup> in which the rate constant  $k_{1b}$  is given by (neglecting H-atom abstraction from the  $-CH_3$ ,  $-CH_2$ and -OH groups; see below),

$$k_{1\mathrm{b}} = k_{\mathrm{tert}} F(-\mathrm{OH})F(\mathrm{X})F(\mathrm{Y}) \tag{II}$$

where  $k_{\text{tert}}$  is the rate constant for H-atom abstraction from a CH- group, and F(-OH), F(X) and F(Y) are the substituent group factors for the three groups attached to the tertiary carbon atom. The groups X and Y are  $-CH_3$  and  $-CH_3$  for propan-2-ol,  $-CH_3$  and  $-CH_2$ — for butan-2-ol, and  $-CH_2$ — and  $-CH_2$ — for heptan-4-ol, and Atkinson<sup>4</sup> and Aschmann and Atkinson<sup>31</sup> have estimated that  $F(-CH_2-)/F(-CH_3) \approx 1.5-1.67$  at room temperature. The rate constants  $k_1$  given above for propan-2-ol, butan-2-ol and heptan-4-ol are consistent with these estimates and, using  $k_{tert}$  $\approx 8 \times 10^{-17}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> <sup>4,31</sup> and neglecting H-atom abstraction from the  $-CH_3$  and  $-CH_2$ — groups<sup>4,31</sup> in these secondary alcohols, a value of  $F(-OH) \approx 15-20$  is derived from our data. It is likely that H-atom abstraction from the  $-CH_2OH$  groups in the alcohols studied is the sole pathway for the NO<sub>3</sub> radical reactions with primary and secondary alcohols, and that the occurrence of a reaction with N<sub>2</sub>O<sub>5</sub> is the reason for the less than unit carbonyl yields measured. In that case, the rate constants  $k_{1b}$  are also the rate constants  $k_1$  for the overall reactions of the NO<sub>3</sub> radical with the primary and secondary alcohols studied.

#### **Reactions with chloroalkenes**

The rate constants  $k_1$  obtained here for *cis*-1,2-dichloroethene, 1,1-dichloroethene, trichloroethene, tetrachloroethene and 3chloropropene (the latter relative to the rate constants for the NO<sub>3</sub> radical reactions with 2,3-dimethylbutane and propene) are given in Table 4. As noted above, the rate constants for cis-1,2-dichloroethene, trichloroethene and tetrachloroethene are only of semi-quantitative quality, and only an upper limit is cited for the tetrachloroethene rate constant. However, as seen from Table 4, our rate constants for cis-1,2-dichloroethene. trichloroethene and tetrachloroethene are consistent with the literature data, and our rate constant for 1,1dichloroethene is in good agreement with the absolute and relative rate data of Noremsaune et al.,22 but somewhat higher than the relative rate constants of Atkinson et al.<sup>18</sup> and Noremsaune et al.<sup>20</sup> and the absolute rate constant of Cabañas Galan et al.<sup>21</sup> For the reaction of the NO<sub>3</sub> radical with 3-chloropropene, our rate constants relative to 2,3dimethylbutane and propene are in agreement [the rate constant relative to propene has significant uncertainties because the rate constant ratio  $k_1$ (3-chloropropene)/ $k_2$ (propene) is < 0.1 and only a small fraction of the initial 3-chloropropene reacted], and agree well with the previous measurement of Atkinson et al.<sup>18</sup> from this laboratory measured relative to the rate constant for the reaction of the NO<sub>3</sub> radical with ethene. However, our present and previous<sup>18</sup> relative rate constants, obtained using three different reference compounds, are a factor of ca. 8-10 lower than the absolute rate constant measured by Martinez et al.15 There is no obvious reason for this discrepancy, although a chain reaction initiated by Cl atoms in the discharge flow study<sup>15</sup> may account, at least in part, for this discrepancy. Further absolute measurements of the rate constants for the reactions of the NO3 radical with 3chloropropene, 3-bromopropene and 3-iodopropene are clearly needed.

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