

# Kinetic study of OH and NO<sub>3</sub> radical reactions with 14 aliphatic aldehydes†

Barbara D'Anna, Øyvind Andresen, Ziv Gefen and Claus J. Nielsen\*

Department of Chemistry, University of Oslo, P. O. Box 1033 Blindern, N-0315 Oslo, Norway.  
E-mail: claus.nielsen@kjemi.uio.no

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Rate coefficients for the reactions of NO<sub>3</sub> and OH radicals with 14 aliphatic C2 to C6 aldehydes in purified air at 298 ± 2 K and 1.00 ± 0.01 atm have been determined by the relative rate method using a static reactor equipped with long-path FTIR detection. The aldehydes studied comprise: C2—acetaldehyde; C3—propanal; C4—butanal and 2-methylpropanal; C5—pentanal, 2-methylbutanal, 3-methylbutanal and 2,2-dimethylpropanal; C6—hexanal, 2-methyl-pentanal, 3-methylpentanal, 4-methylpentanal, 3,3-dimethylbutanal, and 2-ethylbutanal. The new data establish that the gas-phase reactivity of aliphatic aldehydes towards the NO<sub>3</sub> and OH radicals follow the linear free energy relationship typical of addition reactions although the net result of the reactions is a H-abstraction. The experiments also indicate that more than 95% of the room temperature NO<sub>3</sub> reaction with aliphatic aldehydes proceeds through an abstraction of the aldehydic hydrogen. The structure activity relationship for estimation of rate coefficients of the NO<sub>3</sub> radical reaction with saturated organics (*J. Phys. Chem. Ref. Data*, 1991, **20**, 45) fails completely for aliphatic aldehydes.

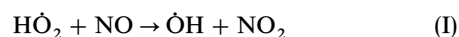
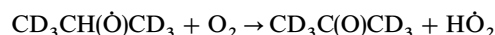
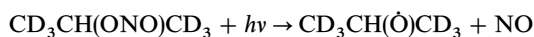
## Introduction

Aldehydes are ubiquitous key components in the chemistry of the troposphere. They are common primary pollutants from biogenic emissions and in residues of incomplete combustion.<sup>1</sup> Relevant natural sources are vegetation, forest fires and microbiological processes.<sup>2</sup> Aldehydes are also nearly mandatory intermediates in the photo-oxidation processes of most organic compounds in the troposphere.<sup>3,4</sup> High concentrations are measured in polluted urban areas as a consequence of the elevated anthropogenic emissions of aldehydes and their precursors from automobile traffic, industrial and domestic heating, and industrial activity.<sup>3,5</sup> The atmospheric loss processes include photolysis, day-time reaction with OH radicals and with Cl and Br atoms in the marine boundary layer, and reaction with NO<sub>3</sub> radicals during the night-time. The photolytic cleavage of aldehydes constitutes an important source of free radicals, particularly in moderately and strongly polluted areas.<sup>3,5</sup> Aldehydes are toxic compounds themselves, and some of their photo-oxidation products, the peroxyacynitrates, are phytotoxic and strong eye-irritant compounds.<sup>3,6</sup> Further, peroxyacynitrates, such as peroxyacetylnitrate (PAN), are long-lived species, which can act as a NO<sub>2</sub> reservoir in the troposphere.

Correlation between the rate coefficients of NO<sub>3</sub> reactions and those of the analogous OH reactions has been demonstrated.<sup>7,8–9</sup> The present systematic investigation was undertaken because the gas-phase reactivity of aldehydes towards OH and NO<sub>3</sub> radicals apparently deviated from the expected linear free energy relationship typical of H-abstraction reactions.<sup>10</sup> A preliminary account of the present study has been presented as part of the EUROTRAC-2 project “Chemical Mechanism Development”, CMD.<sup>11</sup>

## Experimental

The experiments were performed in synthetic air (AGA plus; CO and NO<sub>x</sub> < 100 ppb, C<sub>n</sub>H<sub>m</sub> < 1 ppm) at 298 ± 2 K and 1013 ± 10 mbar in a 250 L electropolished stainless-steel reactor equipped with a White type multiple reflection mirror system of 120 m optical path length for on-line FTIR detection. Infrared spectra were recorded with a Bruker IFS 88 employing a nominal resolution of 0.5 cm<sup>−1</sup>, Harp–Genzel apodization and adding 100 scans; the time of registration was ca. 60 s. The NO<sub>3</sub> radicals were generated *in situ* by thermal dissociation of N<sub>2</sub>O<sub>5</sub>. The hydroxyl radicals were generated by photolysis of different organic nitrites (CH<sub>3</sub>ONO, 2-propylnitrite, 2PN, and 2-propylnitrite-d<sub>6</sub>, 2PN-d<sub>6</sub>) employing Philips TLD-08 fluorescence lamps (λ<sub>max</sub> ~ 370 nm) mounted in a quartz tube and inserted into the reaction chamber; the lamps were turned off during registration of the spectra. 2PN has the advantage over n-alkyl nitrites in that it forms a less reactive compound (acetone) in near quantitative yield following photolysis. 2PN-d<sub>6</sub> has an additional advantage: both itself and its photolysis product do not absorb infrared radiation in the spectral regions used to analyse the kinetics and to analyse for products.



N<sub>2</sub>O<sub>5</sub> was synthesised by mixing gas streams of O<sub>3</sub> and NO<sub>2</sub>, trapping the products at −78 °C. N<sub>2</sub>O<sub>5</sub> was purified by vacuum distillation prior to its use. Methylnitrite, 2-propylnitrite and 2-propyl-nitrite-1,1,1,3,3,3-d<sub>6</sub> were prepared from the alcohols following the procedure reported for butyl nitrite.<sup>12</sup> 2-propanol-1,1,1,3,3,3-d<sub>6</sub> was prepared from acetone-d<sub>6</sub> by reduction with LiAlH<sub>4</sub> in dry ether.

All the aldehydes employed in the relative rate experiments had a stated purity of 95% or better and were used without

† Electronic Supplementary Information available. See <http://www.rsc.org/suppdata/cp/b1/b103623h/>

further purification: acetaldehyde, propanal, butanal, pentanal, hexanal, 2-methylpropanal, 2,2-dimethylpropanal, 2-methylpentanal (Fluka), 3,3-dimethylbutanal (Aldrich), 2-methylbutanal, 3-methylbutanal, 3-methylpentanal, 4-methylpentanal and 2-ethylbutanal (Acros). Propene (Aldrich) and but-1-ene (Fluka) were used as reference compounds. Typical volume fractions were 1–3 ppm for the aldehydes and reference compounds and 5–20 ppm for CH<sub>3</sub>ONO, 2PN, 2PN-d<sub>6</sub> and N<sub>2</sub>O<sub>5</sub>.

The chemical and photochemical stability of reference compounds and aldehydes in the reaction chamber was investigated separately; the compounds showed lifetimes in the order of days and wall-loss or direct photolysis could thus be neglected in the data analyses.

## Results

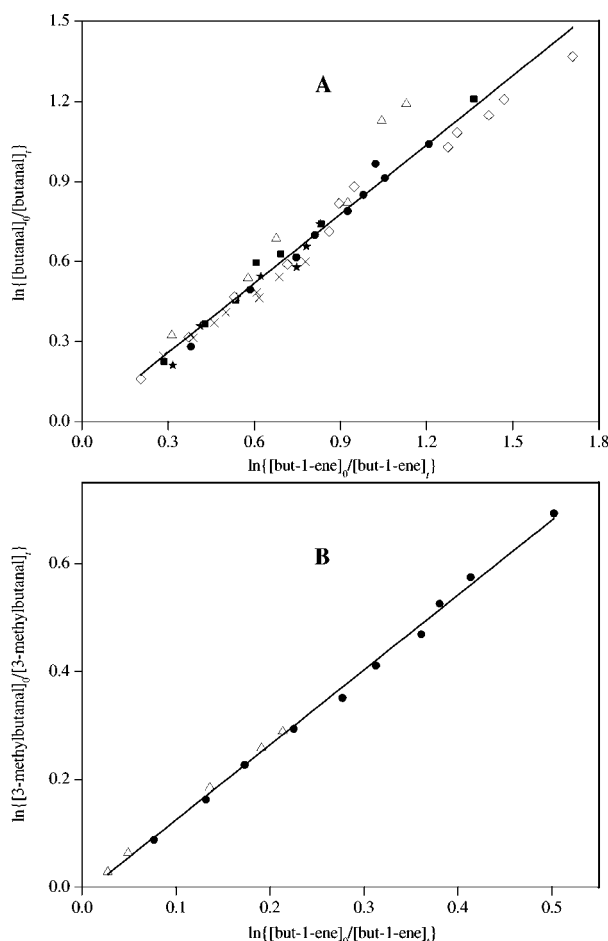
The NO<sub>3</sub> and OH reaction rate coefficients were determined by the “relative rate” method, that is by considering two competing bimolecular reactions with the rate coefficients,  $k_{\text{Ref}}$  and  $k_{\text{Ald}}$ . Assuming that there are no other loss processes for the aldehyde and the reference compound, then the following relation is obtained:

$$\ln \left\{ \frac{[\text{Ald}]_0}{[\text{Ald}]_t} \right\} = \frac{k_{\text{Ald}}}{k_{\text{Ref}}} \times \ln \left\{ \frac{[\text{Ref}]_0}{[\text{Ref}]_t} \right\} \quad (1)$$

where [Ald]<sub>0</sub>, [Ald]<sub>t</sub>, [Ref]<sub>0</sub> and [Ref]<sub>t</sub> denote the concentrations of the aldehyde and the reference at time zero and *t*, respectively. A plot of  $\ln\{[\text{Ald}]_0/[\text{Ald}]_t\}$  vs.  $\ln\{[\text{Ref}]_0/[\text{Ref}]_t\}$  will give the ratio  $k_{\text{Ald}}/k_{\text{Ref}}$  as the slope. The ratio between the concentrations of the aldehydes and the reference compounds was found by spectral subtraction using authentic spectra of the pure starting compounds, spectra of other compounds identified in the reaction mixture and a sloping background. The spectral ranges and the compounds included in the subtraction procedures are available as Electronic Supplementary Information.† Propene was used as the reference compound in the studies of propanal, in all the other experiments but-1-ene was used.

For each compound the data from several independent experiments were analysed jointly according to eqn. (1) using a weighted least squares procedure including uncertainties in both reactant concentrations and allowing a zero-point offset.<sup>13</sup> Examples of the plots of  $\ln\{[\text{Ald}]_0/[\text{Ald}]_t\}$  vs.  $\ln\{[\text{Ref}]_0/[\text{Ref}]_t\}$  are shown in Fig. 1 and 2 for the NO<sub>3</sub> and OH experiments, respectively, while Table 1 summarises the results obtained; the error limits quoted on the present results correspond to 3σ from the statistical analyses and include neither uncertainties in the reaction rate coefficients of the reference compounds nor possible systematic errors in the experiments. The complete data set is available as Electronic Supplementary Information.†

As an example of the spectral subtraction, Fig. 3 shows the relevant parts of the infrared spectra of the NO<sub>3</sub>/3-methylbutanal/but-1-ene system at different times of reaction (starting volume fractions: 3 ppm 3-methylbutanal, 3 ppm but-1-ene, 10 ppm N<sub>2</sub>O<sub>5</sub>). Fig. 3 also includes the spectra of the additional compounds used in the spectral subtraction as well as the residual spectra (this particular example is chosen because our result for this reaction shows the largest deviation from previous results). As can be seen from the residues, the spectra of the reaction mixture can be accounted for to a high degree. In numbers the residuals constitute a spectral rms noise of less than 0.0006 and 0.001 absorbance units in the C–H<sub>ald</sub> and the =CH<sub>2</sub> antisymmetric stretching regions, respectively. This is about 1–2% of the band intensities in the last spectra included in the analysis. The main reaction path of the NO<sub>3</sub> and OH initiated oxidation processes is aldehydic H-abstraction.<sup>26</sup> As there is always ample NO<sub>2</sub> present in the

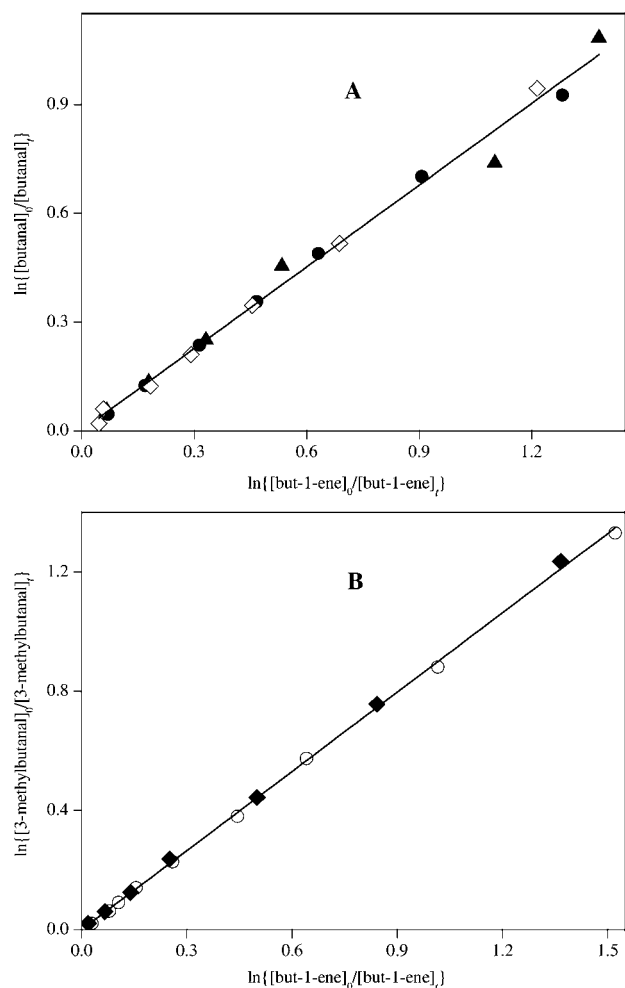


**Fig. 1** Plots of  $\ln\{[\text{Ald}]_0/[\text{Ald}]_t\}$  vs.  $\ln\{[\text{Ref}]_0/[\text{Ref}]_t\}$  for the decays of aldehydes and reference compounds during reaction with NO<sub>3</sub>. Different symbols indicate independent experiments. Errors quoted are the 3σ statistical errors. (A) Butanal: 49 data points, four experiments,  $k_{\text{rel}} = 0.91 \pm 0.08$ ; (B) 3-methylbutanal: 15 data points, two experiments,  $k_{\text{rel}} = 1.38 \pm 0.06$ .

reactor the formation of the quite stable C<sub>n</sub> peroxyacylnitrates partly blocks the subsequent decarboxylation to either C<sub>n-1</sub> aldehydes or ketones. The IR spectra of the compounds studied are sufficiently different to ensure reliable spectral subtractions,<sup>10</sup> provided all the relevant spectra are included.

The regioselectivity of the NO<sub>3</sub> reactions with aldehydes is illustrated in Fig. 4 showing the IR spectrum of the C–H<sub>ald</sub> stretching region of butanal during reaction with NO<sub>3</sub> (starting volume fractions: 10 ppm butanal, 40 ppm N<sub>2</sub>O<sub>5</sub>). The figure includes reference spectra of propane, nitric acid, and the (expanded) residual spectrum of the reaction mixture obtained after spectral subtraction of butanal, propanal and nitric acid. The amount of propanal present in the reaction mixture after 15 min of reaction, found by spectral subtraction using curve b in Fig. 4, was only ca. 2% of the reacted butanal. As can be seen, there is no trace of any other (substituted) aldehyde in the residual spectrum, which is essentially “noise” with a rms value of less than 2% of the butanal band. The spectra suggest that the remaining ca. 98% of the reacted butanal is tied up as peroxyhydrate.

In the experiments the random “experimental” errors arise from temperature fluctuations and from the quantitative determination of relative reactant concentrations by spectral subtraction. These errors are reflected in the statistical error from the least-squares analysis and amount to less than ±10% (3σ) in all cases. In addition, we may have systematic errors due to competing reactions in the smog chamber. That is, in the NO<sub>3</sub> studies OH radicals may be produced from HO<sub>2</sub> (HO<sub>2</sub> + NO<sub>3</sub> → OH + NO<sub>2</sub> + O<sub>2</sub>).<sup>14</sup>

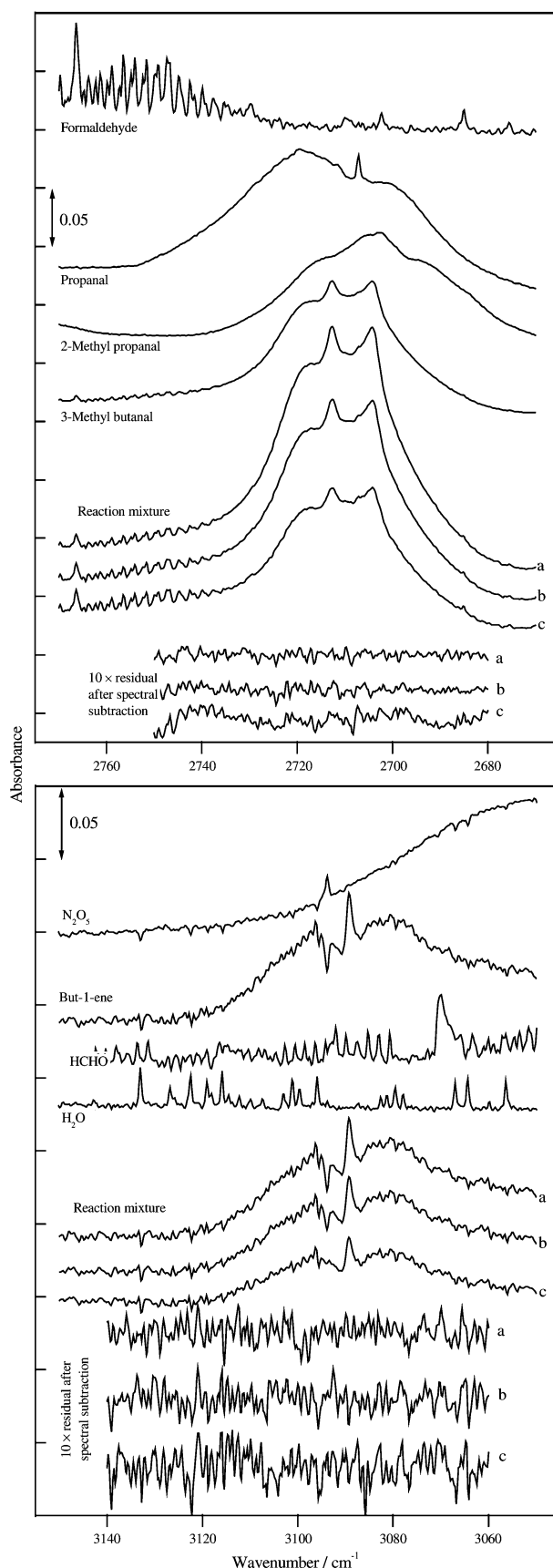


**Fig. 2** Plots of  $\ln\{[\text{Ald}]_0/[\text{Ald}]_t\}$  vs.  $\ln\{[\text{Ref}]_0/[\text{Ref}]_t\}$  for the decays of aldehydes and reference compounds during reaction with OH. Different symbols indicate independent experiments. Errors quoted are the  $3\sigma$  statistical errors. (A) Butanal: 20 data points, three experiments,  $k_{\text{rel}} = 0.76 \pm 0.05$ ; (B) 3-methylbutanal: 16 data points, two experiments,  $k_{\text{rel}} = 0.889 \pm 0.023$ .

We have recently shown that at the experimental conditions in our reaction chamber (see experimental) the influence of such systematic errors in the derived rate coefficients is negligible for the  $\text{NO}_3$ /acetaldehyde system.<sup>27</sup> The same should be valid for the other systems studied as well. Thus the derived relative rate coefficients are believed to be accurate within  $\pm 10\%$ .

## Discussion

As evident from Table 1, the determined rate coefficients for the  $\text{NO}_3$  radical reactions with aliphatic aldehydes are in good agreement with previous results. Only in the case of 3-methyl butanal does the rate coefficient disagree considerably with the value of Glausius *et al.*<sup>22</sup> We find no obvious systematic or analytic errors in our results, Fig. 3, and suggest the present data to be preferred. The rate coefficients for the OH radical reactions with the aliphatic aldehydes, Table 1, are also in good agreement with the majority of the previous studies although considerable disagreement is observed on comparison with the values published by Audley *et al.*,<sup>18</sup> Dobé *et al.*<sup>20</sup> and Glausius *et al.*<sup>22</sup> The latter two data sets have relatively large uncertainties and generally the OH reaction rate coefficients of Audley *et al.*<sup>18</sup> and Dobé *et al.*<sup>20</sup> are too low and too high, respectively, compared with other results. In any case, our data set is in general agreement with



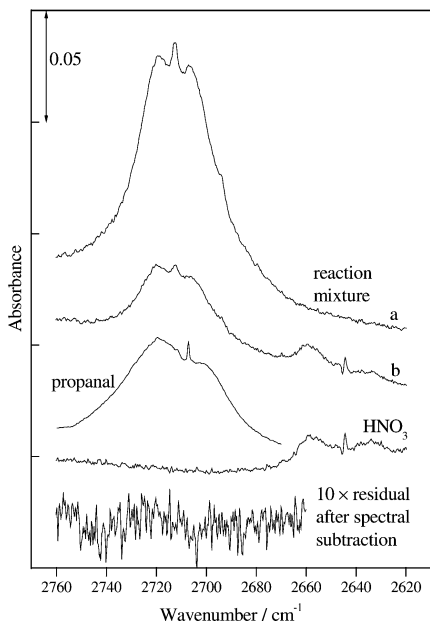
**Fig. 3** Infrared spectra of the  $\text{C-H}_{\text{ald}}$  stretching region (2770–2670  $\text{cm}^{-1}$ ) and the  $=\text{CH}_2$  antisymmetric stretching region (3150–3050  $\text{cm}^{-1}$ ) of the  $\text{NO}_3$ /3-methyl butene/but-1-ene system during reaction. Spectrum of the reaction mixture after 3 min (a), after 10 min (b) and after 40 min (c). Starting volume fractions: 3 ppm 3-methyl butanal, 3 ppm but-1-ene, 10 ppm  $\text{N}_2\text{O}_5$ .

**Table 1** Rate coefficients for the gas phase reactions of NO<sub>3</sub> and OH radicals with aliphatic aldehydes at 298 ± 2 K

NO <sub>3</sub> reactions					OH reactions							
Cn	#	Aldehyde	$k_{\text{Alid}}/k_{\text{ref}}$	Reference compound <sup>a</sup>	$k_{\text{NO}_3}/10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Method <sup>b</sup>	Ref.	$k_{\text{Alid}}/k_{\text{ref}}$	Reference compound	$k_{\text{OH}}/10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Method	Ref.
C1:	1	Formaldehyde			0.058 ± 0.017	Review	14			0.92 ± 0.09	Review	14
	2	Acetaldehyde	0.194 ± 0.021	But-1-ene	0.26 ± 0.03	RR-FTIR	This work	0.458 ± 0.024	But-1-ene	1.44 ± 0.07	RR-FTIR	14
	3	Propanal	0.65 ± 0.06	Propene	0.27 ± 0.05	Review	14	0.72 ± 0.06	Propene	1.60 ± 0.16	Review	14
C3:	3	Propanal		Methacrolein	0.62 ± 0.06	RR-GC	15			1.90 ± 0.15	RR-FTIR	This work
	4	Butanal	0.91 ± 0.08	But-1-ene	0.57 ± 0.04	RR-FTIR	10			2.00 ± 0.30	Review	14
	4	Butanal		But-1-ene	1.22 ± 0.10	RR-FTIR	This work	0.76 ± 0.05	Methyl vinyl ketone	2.02 ± 0.14	RR-GC	15
C4:	4	Butanal		Methacrolein	1.12 ± 0.05	RR-GC	15			2.38 ± 0.15	RR-FTIR	This work
	4	Butanal		Propene	1.00 ± 0.10	RR-FTIR	16			2.30 ± 0.25	Review	14
	4	Butanal		Propene	1.20 ± 0.10	FFD	16			2.47 ± 0.15	RR-GC	15
C5:	5	2-Methylpropanal	0.93 ± 0.10	But-1-ene	1.09 ± 0.08	RR-FTIR	10					
	5	2-Methylpropanal		Propene	1.26 ± 0.14	RR-FTIR	This work	0.85 ± 0.07	But-1-ene	2.65 ± 0.21	RR-FTIR	This work
	5	2-Methylpropanal		Propene	1.20 ± 0.20	RR-FTIR	16			2.42 ± 0.33	FP-RF	17
C6:	6	Pentanal	1.27 ± 0.16	But-1-ene	0.90 ± 0.10	FFD	16			2.69 ± 0.52	RR-GC	4
	6	Pentanal		But-1-ene	1.21 ± 0.06	RR-FTIR	10			1.79 ± 0.21	RR-GC	18
	6	Pentanal		But-1-ene	1.46 ± 0.09	RR-FTIR	10			2.60 ± 0.40	PLP-LIF	19
C7:	7	2-Methylbutanal	1.98 ± 0.08	But-1-ene	1.71 ± 0.21	RR-FTIR	This work	0.83 ± 0.04	Dipropyl ether	4.47 ± 1.40	DF-RF	20
	7	2-Methylbutanal		But-1-ene	1.41 ± 0.16	RR-GC	15			2.58 ± 0.07	RR-GC	21
	7	2-Methylbutanal		But-1-ene	1.46 ± 0.09	RR-FTIR	10			2.61 ± 0.14	RR-FTIR	This work
C8:	8	3-Methylbutanal	1.38 ± 0.06	But-1-ene	2.68 ± 0.11	RR-FTIR	This work	1.04 ± 0.03	But-1-ene	3.28 ± 0.09	RR-FTIR	This work
	8	3-Methylbutanal		But-1-ene	1.86 ± 0.08	RR-FTIR	This work	0.889 ± 0.023	But-1-ene	2.79 ± 0.07	RR-FTIR	This work
	8	3-Methylbutanal		But-1-ene	1.30 ± 0.32	RR-FTIR	22			2.58 ± 0.40	FP-RF	17
C9:	9	2,2-Dimethylpropanal	1.92 ± 0.16	But-1-ene	2.59 ± 0.21	RR-FTIR	This work	0.85 ± 0.04	Ethene	2.68 ± 0.11	RR-GC	4
	9	2,2-Dimethylpropanal		But-1-ene	2.29 ± 0.09	RR-FTIR	10			1.89 ± 0.27	RR-GC	18
	9	2,2-Dimethylpropanal		But-1-ene						4.00 ± 0.70	RR-FTIR	22
C10:	10	Hexanal	1.14 ± 0.14	But-1-ene	1.54 ± 0.19	RR-FTIR	This work	0.91 ± 0.04	But-1-ene	2.68 ± 0.12	RR-FTIR	This work
	10	Hexanal		Methacrolein	1.57 ± 0.21	RR-GC	15			3.06 ± 0.44	FP-RF	17
	10	Hexanal		But-1-ene	1.41 ± 0.16	RR-GC	15			0.86 ± 0.10	RR-GC	18
C11:	11	2-Methylpentanal	1.99 ± 0.08	But-1-ene	1.73 ± 0.18	RR-FTIR	10			2.08 ± 0.58	RR-GC	4
	11	2-Methylpentanal		But-1-ene	2.69 ± 0.11	RR-FTIR	This work	1.06 ± 0.07	But-1-ene	3.32 ± 0.21	RR-FTIR	This work
	11	2-Methylpentanal		But-1-ene	2.41 ± 0.08	RR-FTIR	This work	0.93 ± 0.05	Tut-1-ene	2.91 ± 0.15	RR-FTIR	This work
C12:	12	3-Methylpentanal	1.78 ± 0.06	But-1-ene	1.68 ± 0.09	RR-FTIR	This work	0.84 ± 0.03	But-1-ene	2.63 ± 0.11	RR-FTIR	This work
	12	3-Methylpentanal		But-1-ene	1.25 ± 0.07	RR-FTIR	This work	0.68 ± 0.05	But-1-ene	2.14 ± 0.14	RR-FTIR	This work
	12	3-Methylpentanal		But-1-ene	1.71 ± 0.14	RR-FTIR	This work					
C13:	13	4-Methylpentanal	1.27 ± 0.10	But-1-ene	2.00 ± 0.14	RR-FTIR	10					
	13	4-Methylpentanal		But-1-ene	2.00 ± 0.14	RR-FTIR	10					
	13	4-Methylpentanal		But-1-ene	4.46 ± 0.23	RR-FTIR	This work	1.28 ± 0.13	But-1-ene	4.02 ± 0.40	RR-FTIR	This work
C14:	14	3,3-Dimethylbutanal		But-1-ene								
	14	3,3-Dimethylbutanal		But-1-ene								
	14	3,3-Dimethylbutanal		But-1-ene								
C15:	15	2-Ethylbutanal	3.31 ± 0.17	But-1-ene								
	15	2-Ethylbutanal		But-1-ene								
	15	2-Ethylbutanal		But-1-ene								

<sup>a</sup> The reaction rate coefficients for the relative rate studies have been placed on an absolute scale using the following rate coefficients (cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) for the NO<sub>3</sub> and OH reactions:  $k_{\text{propene}+\text{NO}_3} = 9.5 \times 10^{-15}$  (ref. 14),  $k_{\text{but-1-ene}+\text{NO}_3} = 1.35 \times 10^{-14}$  (ref. 24),  $k_{\text{methacrolein}+\text{NO}_3} = 3.3 \times 10^{-15}$  (ref. 14),  $k_{\text{ethene}+\text{OH}} = 7.9 \times 10^{-12}$  at 1 bar (ref. 14),  $k_{\text{propene}+\text{OH}} = 2.9 \times 10^{-11}$  at 1 bar (ref. 14),  $k_{\text{but-1-ene}+\text{OH}} = 3.13 \times 10^{-11}$  (ref. 24),  $k_{\text{dipropyl ether}+\text{OH}} = 1.85 \times 10^{-11}$  (ref. 25),  $k_{\text{isoprene}+\text{OH}} = 1.01 \times 10^{-10}$  (ref. 24). <sup>b</sup> Abbreviations: Review, recommended values from a critical review of kinetic data; RR-FTIR, relative rate-Fourier transform infrared spectroscopy; RR-GC, relative rate-gas chromatography; FFD, fast flow discharge; FP-RF, flash photolysis-resonance fluorescence; FFP-RF, flash photolysis-resonance fluorescence; PLF-LIF, pulsed laser photolysis-laser induced fluorescence.

<sup>a</sup> The reaction rate coefficients for the relative rate studies have been placed on an absolute scale using the following rate coefficients (cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) for the NO<sub>3</sub> and OH reactions:  $k_{\text{propene}+\text{NO}_3} = 9.5 \times 10^{-15}$  (ref. 14),  $k_{\text{but-1-ene}+\text{NO}_3} = 1.35 \times 10^{-14}$  (ref. 24),  $k_{\text{methacrolein}+\text{NO}_3} = 3.3 \times 10^{-15}$  (ref. 14),  $k_{\text{ethene}+\text{OH}} = 7.9 \times 10^{-12}$  at 1 bar (ref. 14),  $k_{\text{propene}+\text{OH}} = 2.9 \times 10^{-11}$  at 1 bar (ref. 14),  $k_{\text{but-1-ene}+\text{OH}} = 3.13 \times 10^{-11}$  (ref. 24),  $k_{\text{dipropyl ether}+\text{OH}} = 1.85 \times 10^{-11}$  (ref. 25),  $k_{\text{isoprene}+\text{OH}} = 1.01 \times 10^{-10}$  (ref. 24). <sup>b</sup> Abbreviations: Review, recommended values from a critical review of kinetic data; RR-FTIR, relative rate-Fourier transform infrared spectroscopy; RR-GC, relative rate-gas chromatography; FFD, fast flow discharge; DF-RF, discharge flow-resonance fluorescence; FP-RF, flash photolysis-resonance fluorescence; PLP-LIF, pulsed laser photolysis-laser induced fluorescence.

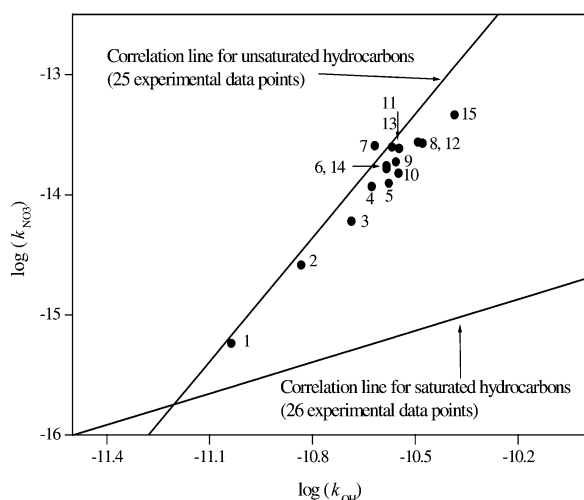


**Fig. 4** Infrared spectra of the C-H<sub>ald</sub> stretching region (2770–2610 cm<sup>-1</sup>) of the NO<sub>3</sub>/butanal system during reaction. Spectrum of the reaction mixture at start (a) and after 15 min (b). Start volume fractions: 10 ppm butanal, 40 ppm N<sub>2</sub>O<sub>5</sub>.

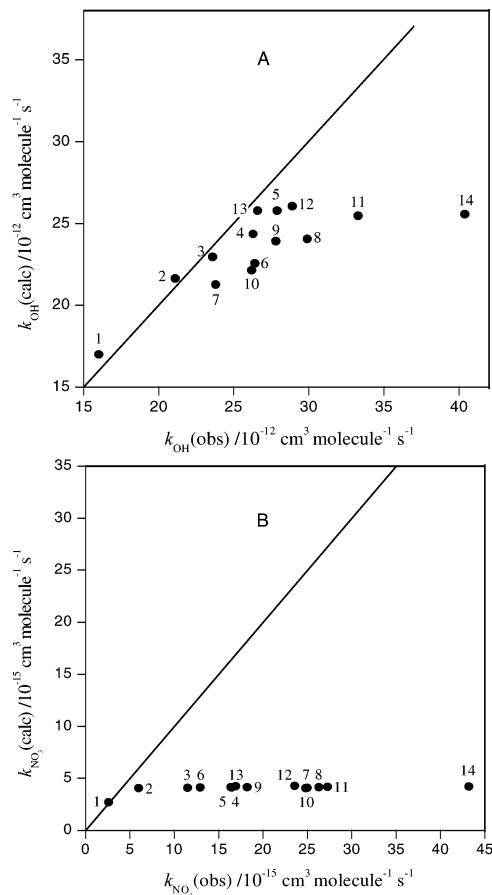
the majority of other results and we consider it as internally consistent and to be preferred.

We have previously shown that the rate coefficients for the H<sub>ald</sub>-atom abstraction by NO<sub>3</sub> and OH radicals correlate.<sup>10,11</sup> The data points, shown in Fig. 5, however, fall close to the correlation line for addition reactions and not close to the correlation line for abstraction reactions (the correlation lines are based on the same compounds as those employed by Wayne *et al.* in their review,<sup>7</sup> but using updated values for the rate coefficients<sup>14,24,25</sup>). To be discussed later, this implies that the OH and NO<sub>3</sub> reactions with aliphatic aldehydes are not just simple, straight H-abstraction reactions.

The structure activity relationship (SAR) for OH radical reactions with hydrocarbons, originally developed by Atkinson and co-workers,<sup>26,28–31</sup> generally reproduces the experi-



**Fig. 5** Log of the rate coefficients at 298 K for the reactions of NO<sub>3</sub> vs. the log of the rate coefficients for reaction of OH with the same substrates. The numbers identifying the individual aldehydes are the same as in Table 1. The correlation line for abstraction reactions is given by:  $\log(k_{\text{NO}_3}) = (0.87 \pm 0.09) \times \log(k_{\text{OH}}) + (-6.0 \pm 1.0)$ . The correlation line for addition reactions is given by:  $\log(k_{\text{NO}_3}) = (3.43 \pm 0.24) \times \log(k_{\text{OH}}) + (22.7 \pm 2.5)$ .

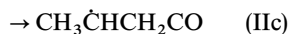
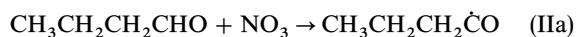


**Fig. 6** (A) Calculated vs. observed reaction rate coefficients at 298 K for the OH reaction with aliphatic aldehydes. The calculation is based on the structure–reactivity by Kwok and Atkinson, ref. 30. (B) Calculated vs. observed reaction rate coefficients at 298 K for the NO<sub>3</sub> reaction with aliphatic aldehydes. The calculation is based on the structure–reactivity by Atkinson, ref. 8. The numbers identifying the individual aldehydes are the same as in Table 1.

mental results within a factor of 2. Fig. 6A shows the correlation between observed and calculated OH reaction rate coefficients for aliphatic aldehydes.<sup>30</sup> As can be seen, the SAR is apparently adequate for estimating the OH radical reactions with aliphatic aldehydes. However, there seems to be a systematic deviation with increasing reactivity. Even for the fastest reacting aldehydes, the reaction rate is still an order of magnitude below the value expected for reaction on every collision. The deviations are therefore not entirely caused by a violation of the underlying assumption in the SAR concept. We suggest that the new OH reaction data for aliphatic aldehydes warrant a revision of the SAR.

Atkinson has also proposed a similar SAR for the NO<sub>3</sub> reactions.<sup>8</sup> Fig. 6B shows the correlation between observed and calculated rate coefficients for NO<sub>3</sub> reactions with aliphatic aldehydes. As can be seen, the method is clearly inadequate for estimating the NO<sub>3</sub> radical reactions with aliphatic aldehydes. The increase of the rate coefficients with the size/chain length of the aldehyde is much more rapid than predicted. A recent study suggests that the observed increase in NO<sub>3</sub> reaction rate constant from propanal to hexanal implies that (i) the CH<sub>2</sub> groups several carbon atoms away from the –CHO group are activated, (ii) the reaction is not a simple H-atom abstraction, or (iii) the estimation method for calculating NO<sub>3</sub> radical reaction rate constants is not accurate.<sup>15</sup> Taking butanal as an example: butanal (molecule #4, Table 1, Fig. 5 and 6) reacts about 4 times faster with NO<sub>3</sub> than according to the SAR model.<sup>8</sup> Assuming that butanal reacts with NO<sub>3</sub> through H-abstraction at positions C2 to C4 in

addition to the H<sub>ald</sub>-abstraction, the following radicals should be formed:



To have an activation of neighbouring CH<sub>x</sub> groups making up for the “additional” reactivity of butanal, would require that channels (IIb–d) should actually dominate over (IIa). That is, one would expect significant amounts of either 2- or 3-oxo butanal or butadiol to be formed as products following the initial H-abstraction in the smog chamber. Unfortunately, the carbonyl stretching region around 1800 cm<sup>−1</sup> is dominated by the strong N<sub>2</sub>O<sub>5</sub> and RO<sub>2</sub>NO<sub>2</sub> bands, and it is not possible to discern any new bands in this region. However, even allowing for a possible increased reactivity of the above-mentioned compounds towards NO<sub>3</sub> compared to that of butanal, one should still be able to see a significant formation of such new (oxo)aldehydes in the C–H<sub>ald</sub> stretching region in the infrared spectra of the reaction mixture. As Fig. 4 clearly demonstrates, this is *not* the case—there is not even a trace of formaldehyde. The spectral results thus show that any additional aldehyde or oxo-aldehyde formed in the reaction contributes very little to the absorbance in the C–H<sub>ald</sub> stretching region of the infrared spectrum. As already mentioned, the residual spectrum (Fig. 4) is essentially “noise” with a rms value of less than 2% of the butanal band. A conservative upper estimate of the methyl and/or methylene H-abstraction channels in butanal by NO<sub>3</sub> will be 5% of the total. We therefore conclude that the increase in the aldehyde/NO<sub>3</sub> reaction rate coefficient with increasing chain length is *not* caused by the suggested activation of nearby CH<sub>x</sub> groups.

It is clear from experimental data<sup>27,32,33</sup> and from theoretical studies<sup>34–38</sup> that both OH and NO<sub>3</sub> react with aldehydes by H-abstraction and not by addition to the π-system. In the case of OH the addition pathway would lead to the formation of organic acids, which have never been identified as products of this reaction. The *ab initio* estimated barrier height to addition is also very high, 30–40 kJ mol<sup>−1</sup>.<sup>35,37</sup> In the case of NO<sub>3</sub>, *ab initio* calculations show that the addition reaction is endothermic.<sup>38</sup> Studies of isotope labelled formaldehyde and acetaldehyde show kinetic isotope effects, which are only consistent with a H<sub>ald</sub>-abstraction.<sup>27,38</sup> In summary, the net results of the OH and NO<sub>3</sub> reactions with aliphatic aldehydes are hydrogen abstractions, and for NO<sub>3</sub> the present results show that more than 95% of the reaction is an abstraction of the aldehydic hydrogen.

It is a fact that the OH reactions with aldehydes apparently show a negative activation energy,<sup>14,17,19,20</sup> while the NO<sub>3</sub> reactions studied show a positive activation energy.<sup>14,16,27</sup> Also the halogen atom reactions with aliphatic aldehydes show a positive activation energy.<sup>14</sup> On the other hand, theoretical studies show that OH,<sup>34–38</sup> NO<sub>3</sub>,<sup>38</sup> and also F, Cl and B<sup>39</sup> all form adducts of various stability with aldehydes, and we attribute the apparent “addition reaction behaviour” of the OH and NO<sub>3</sub> reactions with aldehydes, as manifested in the linear free-energy plot (Fig. 5), to the formation of pre-reaction adducts, while the different temperature behaviour of the radical and atom reactions with the aldehydes is linked to the actual barrier height to the H<sub>ald</sub>-abstraction reaction. In other words, the C–H<sub>ald</sub>-abstraction reactions are not simple bimolecular elementary reactions.

The apparent failure of the estimation method for calculating NO<sub>3</sub> radical reaction rate coefficients<sup>8</sup> is therefore not linked to an underestimation of the activation of adjacent

–CH<sub>2</sub>– groups, but rather to the inductive effects of the alkyl chain on both the stability of the pre-reaction adducts and on the activated complex. We are therefore following up the present experimental study with *ab initio* calculations on the NO<sub>3</sub> reactions with propanal and 2-methyl propanal.

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