

# Reactions of acrolein, crotonaldehyde and pivalaldehyde with Cl atoms: structure–activity relationship and comparison with OH and NO<sub>3</sub> reactions†

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Rate coefficients for the reaction of acrolein (prop-2-en-1-al), crotonaldehyde (but-2-en-1-al) and pivalaldehyde (2,2-dimethylpropanal) with chlorine atoms were determined. The resulting rate coefficients were  $(1.8 \pm 0.3) \times 10^{-10}$ ,  $(2.2 \pm 0.4) \times 10^{-10}$  and  $(1.2 \pm 0.2) \times 10^{-10}$  (cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) for acrolein, crotonaldehyde and pivalaldehyde, respectively. Rate coefficients for chlorine atom reaction with propanal, butanal, 2-methylpropanal and *trans*-but-2-ene were determined to be  $(1.2 \pm 0.2) \times 10^{-10}$ ,  $(1.5 \pm 0.3) \times 10^{-10}$ ,  $(1.5 \pm 0.3) \times 10^{-10}$  and  $(3.0 \pm 0.6) \times 10^{-10}$  (cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>), respectively. The relative rate technique was used with propene as the reference compound. The experiments were carried out at  $297 \pm 2$  K and  $1020 \pm 2$  mbar using a 0.153 m<sup>3</sup> borosilicate glass reactor with long-path FTIR spectroscopy as the analytical tool. Synthetic air and nitrogen were used as bath gases. Literature values of the corresponding hydroxyl and nitrate radical rate coefficients were confirmed. The chemical characteristics of the organic substances have a limited influence on the reactivity with Cl, a larger effect in the OH-case but are decisive for the NO<sub>3</sub> reactions. Introduction of an aldehydic carbonyl group into an unsaturated compound reduces the reactivity of a neighboring double bond for reaction with all three radicals. The unsaturated aldehydes reacting with NO<sub>3</sub> show a rate coefficient that is lower than both the corresponding simple alkene and aliphatic aldehyde, indicating that also the reactivity of the aldehydic hydrogen atom is affected. The results show that during the morning hours, Cl atoms may be the most significant oxidising agent for organic substances in urban coastal air.

## Introduction

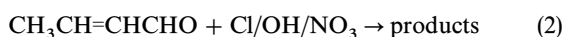
Carbonyl compounds such as carboxylic acids, ketones and aldehydes play an important role in the chemistry of the polluted troposphere. Aldehydes may be emitted as primary pollutants from partial oxidation of hydrocarbon fuels and from biogenic sources. They may also arise as secondary pollutants from atmospheric oxidation of volatile organic compounds (VOC).<sup>1–9</sup> In addition, aldehydes are frequently found in polluted indoor air, *e.g.* ref. 10. Several carbonyls are documented eye irritants and some have toxic and even mutagenic or carcinogenic properties.<sup>8,11–14</sup> Their presence in the environment makes it of considerable interest to find details of their atmospheric transformation processes. The principal unsaturated compounds of atmospheric interest are the  $\alpha,\beta$ -unsaturated carbonyls formed by atmospheric reactions of conjugated dienes, and unsaturated carbonyls formed by reactions of some monoterpenes. Important  $\alpha,\beta$ -unsaturated carbonyls are acrolein, methacrolein, methyl vinyl ketone and crotonaldehyde. Acrolein is formed from atmospheric degradation of buta-1,3-diene<sup>15–17</sup> but can also be emitted with gasoline and diesel exhaust and by combustion processes.<sup>8</sup> Acrolein is also a large industrial commodity since it is an intermediate in the manufacturing of acrylic acid and its derivatives.

Chemical removal of aldehydes from the troposphere can occur by gas phase reaction with OH and NO<sub>3</sub> radicals, with Cl atoms or by photolysis. The hydroxyl radical reaction is

normally the main sink for these compounds during daytime and the nitrate radical plays a role in the night-time chemistry. Chlorine atoms can contribute significantly in the removal process in marine air masses.<sup>18</sup> Photolysis is sometimes an efficient sink process for aldehydes. Acrolein, as an example, has a tropospheric lifetime with respect to photolysis, at a solar zenith angle of 40°, of approximately 10 d<sup>19</sup> while crotonaldehyde has a lifetime of 1.1 d. The latter lifetime was given by ref. 20 for a solar zenith angle of 22.5° but was recalculated to 40° for comparison. In spite of the fact that a considerable number of rate coefficients for atmospheric reactions have been determined during the past decades, for practical reasons it is not possible to study every compound that can be found *e.g.* in the polluted troposphere. It is therefore of value to be able to predict a rate coefficient. At present, it is often possible to estimate rate coefficients for simple compounds within a factor of two, based on the chemical structure of the substance. No method of estimating Cl and NO<sub>3</sub> rate coefficients for more complicated molecules, *e.g.* unsaturated carbonyls, currently exists. Kinetic data for Cl/OH/NO<sub>3</sub> reactions with a larger series of aldehydes than is presently available are thus needed to develop reliable structure–reactivity relationships.

This paper presents results from laboratory kinetic studies of the reaction of acrolein (prop-2-en-1-al), crotonaldehyde (but-2-en-1-al) and pivalaldehyde (2,2-dimethylpropanal) with Cl atoms [reactions (1)–(3)]. In order to ascertain a consistent set of experimental data, a re-determination of the rate coefficients for the reactions of these aldehydes with OH and NO<sub>3</sub> was also made.

† Electronic Supplementary Information available. See <http://www.rsc.org/suppdata/cp/b0/b007244n/>



Pivalaldehyde was included in this study for structural reasons. In order to obtain additional information for a qualitative structure *vs.* reactivity discussion, we also determined the rate coefficients for reaction of chlorine atoms with propanal, butanal, 2-methylpropanal and *trans*-but-2-ene.

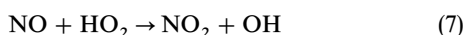
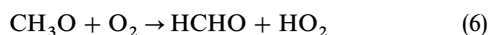
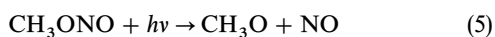
## Experimental section

All experiments were performed in a 0.153 m<sup>3</sup> borosilicate cylindrical glass reactor with a 2 m base-path White optical system. General features of the set-up have previously been described.<sup>21</sup> The system is connected to a Nicolet Magna 560 FTIR spectrometer equipped with an MCT (HgCdTe) detector. All infrared spectra were collected at 1.0 cm<sup>-1</sup> spectral resolution, averaging 64 scans at 1 scan s<sup>-1</sup> and using a 40 m optical pathlength. Desired amounts of reference and studied compounds were metered using a vacuum line and volume-pressure measurement. They were introduced into the reactor by a stream of bath gas (nitrogen or synthetic air). The gases are evenly distributed in the reactor by a Teflon line with nozzles, connected to the gas-inlet and placed along the axis of the reactor. The arrangement promotes mixing of the gases inside the reaction chamber. Reaction mixtures in the reactor can be photolyzed by four 100 W Philips RUV-A lamps with a maximum light intensity at ~350 nm.

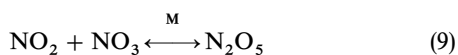
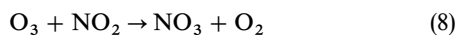
Chlorine atoms were generated by photolysis of molecular chlorine.



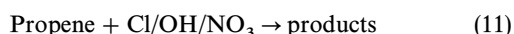
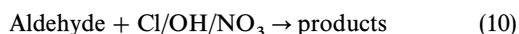
Hydroxyl radicals were generated by photolysis of methyl nitrite in the presence of molecular oxygen, according to reactions (5)–(7).



Methyl nitrite was synthesized by dropwise addition of 50% H<sub>2</sub>SO<sub>4</sub> to methanol saturated with sodium nitrite.<sup>22</sup> The product was collected in a trap cooled by an ethanol–dry ice bath and was stored at 193 K between runs. Nitrate radicals were generated by thermal decomposition of N<sub>2</sub>O<sub>5</sub> which was synthesized in a separate set-up by the reaction of NO<sub>2</sub> with excess O<sub>3</sub> according to reactions (8) and (9). The gas phase synthesis of N<sub>2</sub>O<sub>5</sub> is a modification of a procedure described in the literature using ozone and NO.<sup>23</sup>



Rate coefficients for the reaction between the studied aldehydes and Cl, OH and NO<sub>3</sub> were determined in relative rate experiments using propene as the reference compound. Both nitrogen and synthetic air were used as the bath gas except for the OH experiments where only synthetic air was used. The radical reacts with the aldehyde (10), with an unknown rate coefficient, *k*<sub>ald</sub>, and with the reference compound (11) also present in the reactor, with a known rate coefficient, *k*<sub>propene</sub>.



Provided that both compounds are lost solely by reactions (10) and (11) and neither the aldehyde nor propene is reformed in any process, then the loss of organic compound is given by eqn. (I).<sup>24</sup>

$$\ln \frac{[\text{aldehyde}]_0}{[\text{aldehyde}]_t} = \frac{k_{\text{ald}}}{k_{\text{propene}}} \times \ln \frac{[\text{propene}]_0}{[\text{propene}]_t} \quad (\text{I})$$

Subscripts 0 and *t* indicate concentration at the beginning of an experiment and at time *t*. As the ratios of concentrations are used, IR absorbances may be used directly instead of the absolute concentrations if Beer's law is obeyed. The linearity between IR absorption and concentration was confirmed for each compound used in the experiments. Scaled spectral subtraction, using calibrated reference spectra of the neat compounds at known concentrations, was used for the evaluation. The rate coefficient, *k*<sub>ald</sub>, was obtained from the slope of a line, fitted by the method of least-squares, to a plot of ln([aldehyde]<sub>0</sub>/[aldehyde]<sub>*t*</sub>) *vs.* ln([propene]<sub>0</sub>/[propene]<sub>*t*</sub>), and the literature value of *k*<sub>propene</sub>. The following reference values were used: *k*(propene + Cl) = (2.3 ± 0.4) × 10<sup>-10</sup>,<sup>25</sup> *k*(propene + OH) = (2.9 ± 0.2) × 10<sup>-11</sup>,<sup>26</sup> and *k*(propene + NO<sub>3</sub>) = (9.4 ± 1.2) × 10<sup>-15</sup> (ref. 27) (cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>).

All experiments were performed at 297 ± 2 K and 1020 ± 2 mbar and initial concentrations of the organic compounds were between 1.1 × 10<sup>14</sup> and 1.8 × 10<sup>14</sup> in units of molecule cm<sup>-3</sup>. Initial concentrations of chlorine, methyl nitrite and N<sub>2</sub>O<sub>5</sub> were (5.9–7.2) × 10<sup>14</sup>, (3.9–4.5) × 10<sup>14</sup> and (3.9–4.5) × 10<sup>14</sup> (molecule cm<sup>-3</sup>), respectively. A set of experiments was carried out to establish that there was no significant dark reaction between molecular chlorine and the organic substances used (Table S1, Electronic Supplementary Information†).

All chemicals used were obtained from commercial sources: acrolein 90% (Aldrich), crotonaldehyde 99 + % predominant *trans* (Aldrich), pivalaldehyde 97% (Aldrich), H<sub>2</sub>SO<sub>4</sub> p.a. 96% (Merck), methanol p.a. 99.8% (Merck), sodium nitrite p.a. (Merck), synthetic air (20% O<sub>2</sub> in N<sub>2</sub> > 99.995%), nitrogen > 99.995%, propene 99.5%, chlorine 5.00% in 99.995% helium, nitrogen dioxide ~99%, oxygen > 99.995% (gases from AGA Gas AB). All gases were used as received. Liquid chemicals were subjected to repeated freeze–pump–thaw cycles before use.

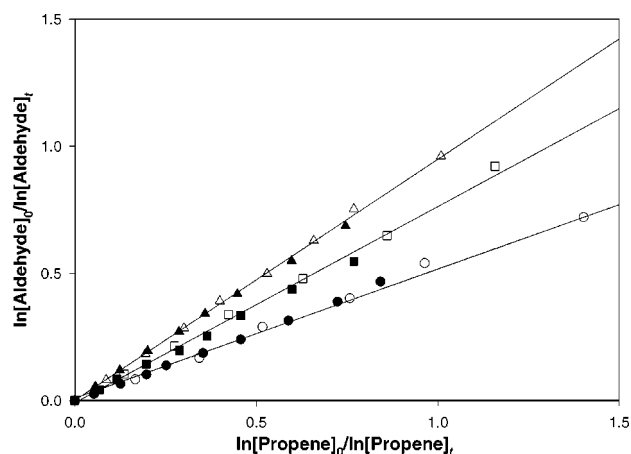
## Results and discussion

### Rate coefficients

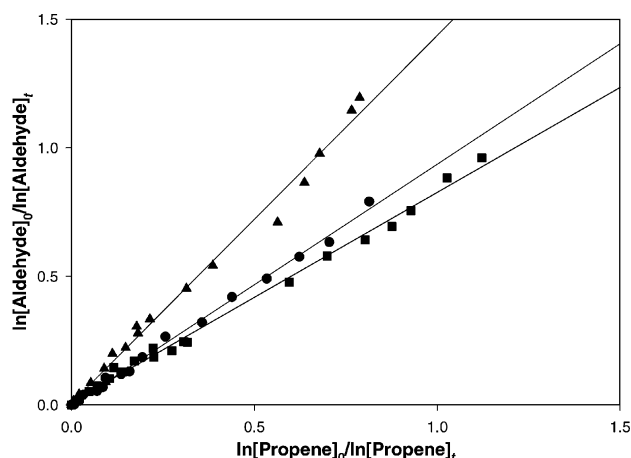
The relative rate plots from the experiments according to eqn. (I) are presented in Fig. 1–3. The resulting rate coefficients are given in Table 1 together with results from previous studies for comparison. The error limits for the relative rate measurements are the 95% confidence intervals from the linear least-squares fitting procedure combined with the uncertainty of the reference rate coefficient. The results from experiments with air and nitrogen as bath gas are identical as can be seen in Fig. 1–3. The intercepts of the straight lines are all equal to zero, within the error limit. These facts, together with the straight lines obtained in the evaluations, indicate that there is no interference from other competing reactions in the systems.

Aldehydes can be photolyzed by actinic UV-radiation. A set of experiments was conducted to establish photolytic loss under typical experimental conditions. Pivalaldehyde and acrolein did not show any measurable photolytic loss rate while the value found for crotonaldehyde was 1.7 × 10<sup>-6</sup> s<sup>-1</sup>. The data for crotonaldehyde reacting with OH radicals were therefore corrected with respect to loss by photolysis for a total time of 10 min in 1 min intervals. The photolysis time required to produce chlorine atoms was short (up to a total of 3 min in 20 s steps) and no corrections were made in this case.

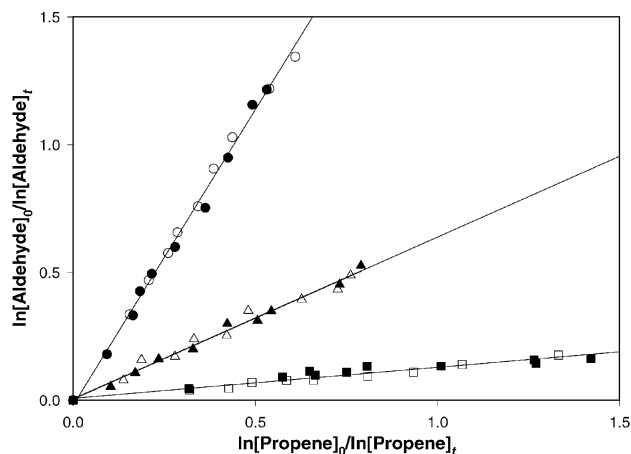
Relative rate experiments were also performed for propanal, butanal, 2-methylpropanal and *trans*-but-2-ene with Cl atoms



**Fig. 1** Plot of  $\ln([aldehyde]_0/[aldehyde]_t)$  vs.  $\ln([propene]_0/[propene]_t)$  from the chlorine atom experiments at  $297 \pm 2$  K and  $1020 \pm 2$  mbar. Maximum total reaction time of 3 min. Squares, triangles and circles represent acrolein, crotonaldehyde and pivalaldehyde, respectively. The closed symbols represent experiments with synthetic air and the open symbols with nitrogen as bath gas.



**Fig. 2** Plot of  $\ln([aldehyde]_0/[aldehyde]_t)$  vs.  $\ln([propene]_0/[propene]_t)$  from the hydroxyl radical experiments in synthetic air at  $297 \pm 2$  K and  $1020 \pm 2$  mbar. Maximum total reaction time of 10 min. Squares, triangles and circles represent acrolein, crotonaldehyde and pivalaldehyde, respectively.



**Fig. 3** Plot of  $\ln([aldehyde]_0/[aldehyde]_t)$  vs.  $\ln([propene]_0/[propene]_t)$  from the nitrate radical experiment at  $297 \pm 2$  K and  $1020 \pm 2$  mbar. Maximum total reaction time of 60 min. Squares, triangles and circles represent acrolein, crotonaldehyde and pivalaldehyde respectively. The closed symbols represent experiments with synthetic air and the open symbols with nitrogen as bath gas.

in synthetic air and nitrogen as bath gases, to add to the reactivity *vs.* structure discussion. Plots from these experiments are shown in Fig. 4 and the resulting rate coefficients are given in Table 1.

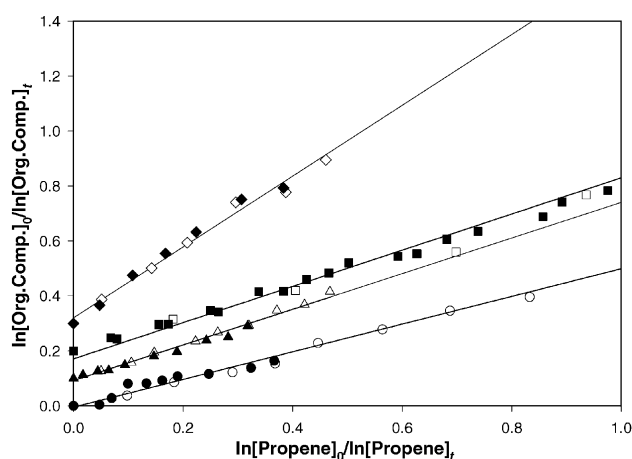
No previous data for any of the Cl rate coefficients determined here were found, and thus, no comparison could be made. The situation is different for OH and NO<sub>3</sub> where several earlier determinations are available (*cf.* Table 1). It appears that our results are in reasonable agreement with the majority of the literature data, something that lends credibility to our experimental procedures. Only two entries in Table 1 have a pronounced difference from the other available determinations. One is the value of  $(8.1 \pm 1.1) \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for the reaction between NO<sub>3</sub> and acrolein.<sup>28</sup> This value should be compared with the other three determinations, all with a value of  $1.1 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The other<sup>41</sup> is a value for the reaction between pivalaldehyde and OH of  $(0.9 \pm 0.1) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> to be compared with the average of the three other determinations of  $(2.6 \pm 1.0) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (the error given is the statistical 2σ).

### Reactivity *vs.* structure

The free radicals responsible for initiating degradation of organic compounds in the atmosphere (*i.e.* Cl, OH and NO<sub>3</sub>) react by two basic mechanisms: abstraction of a hydrogen atom from a C–H bond or addition to a C=C double bond. The initial radical attack is then followed by a series of reactions in air, most often involving organic peroxy radicals, eventually leading to stable products.<sup>43</sup>

Much effort has been made to put the reactivity of a compound in relation to its chemical structure, so-called structure–activity relationships (SAR) *e.g.* ref. 44–49. The concept of predicting rate coefficients by adding group-specific rate coefficients is often used.

For the Cl atom reactions, only hydrogen atom abstraction from alkanes has been discussed so far.<sup>44,45</sup> Ways of predicting OH radical rate coefficients have been proposed for reactions with various classes of hydrocarbons.<sup>47,48</sup> The procedures may handle both saturated and unsaturated hydrocarbons. An attempt to include molecules with various functional groups such as ethers, esters and aldehydes has also



**Fig. 4** Plot of  $\ln([org. compound]_0/[org. compound]_t)$  vs.  $\ln([propene]_0/[propene]_t)$  from the chlorine atom experiments at  $297 \pm 2$  K and  $1020 \pm 2$  mbar. Maximum total reaction time of 3 min. Circles, triangles, squares and diamonds represent propanal, butanal, 2-methylpropanal and *trans*-but-2-ene, respectively. The closed symbols represent experiments with synthetic air and the open symbols with nitrogen as bath gas. Data for butanal, 2-methylpropanal and *trans*-but-2-ene are displaced for clarity on the ordinate by 0.1, 0.2 and 0.3 y-units, respectively.

**Table 1** Rate coefficients ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) for the studied reactions with Cl, OH and  $\text{NO}_3$  at  $297 \pm 2 \text{ K}$  and  $1020 \pm 2 \text{ mbar}$ . Some structurally related compounds are also included

Organic compound	$k_{\text{Cl}}$	Ref.	$k_{\text{OH}}$	Ref.	$k_{\text{NO}_3}$	Ref.
Propene	$(2.3 \pm 0.4) \times 10^{-10}$	25	$(2.9 \pm 0.2) \times 10^{-11}$	26	$(9.4 \pm 1.2) \times 10^{-15}$	27
Acrolein	$(1.8 \pm 0.3) \times 10^{-10}$	This work	$(2.4 \pm 0.2) \times 10^{-11}$	This work	$(1.1 \pm 0.2) \times 10^{-15}$	This work
			$(2.7 \pm 0.3) \times 10^{-11}$	16	$(8.1 \pm 1.1) \times 10^{-15}$	28
			$(1.9 \pm 0.2) \times 10^{-11}$	29	$(1.1 \pm 0.2) \times 10^{-15}$	30 <sup>a</sup>
			$(2.1 \pm 0.1) \times 10^{-11}$	31 <sup>b</sup>	$(1.1 \pm 0.4) \times 10^{-15}$	32
			$(2.04 \pm 0.01) \times 10^{-11}$	33		
Propanal	$(1.2 \pm 0.2) \times 10^{-10}$	This work	$(1.8 \pm 0.1) \times 10^{-11}$	29	$(5.7 \pm 0.4) \times 10^{-15}$	34
<i>Trans</i> -2-Butene	$(3.0 \pm 0.6) \times 10^{-10}$	This work	$(6.1 \pm 0.31) \times 10^{-11}$	35	$(406 \pm 36) \times 10^{-15}$	36
Crotonaldehyde	$(2.2 \pm 0.4) \times 10^{-10}$	This work	$(4.0 \pm 0.3) \times 10^{-11}$	This work	$(6.0 \pm 0.8) \times 10^{-15}$	This work
			$(3.3 \pm 0.6) \times 10^{-11}$	29	$(5.1 \pm 0.2) \times 10^{-15}$	30 <sup>c</sup>
			$(4.0 \pm 0.5) \times 10^{-11}$	31 <sup>b</sup>		
2-Methyl-propanal	$(1.5 \pm 0.3) \times 10^{-10}$	This work	$(2.7 \pm 0.5) \times 10^{-11}$	29	$(12 \pm 2) \times 10^{-15}$	37
Butanal	$(1.5 \pm 0.3) \times 10^{-10}$	This work	$(2.4 \pm 0.1) \times 10^{-11}$	29	$(10 \pm 1) \times 10^{-15}$	37
Pentane	$(2.52 \pm 0.12) \times 10^{-10}$	38	$(0.37 \pm 0.02) \times 10^{-11}$	39	$(0.08 \pm 0.04) \times 10^{-15}$	40
2,2-Di-methylpropane	$(1.10 \pm 0.03) \times 10^{-10}$	38	—	—	—	—
Pivalaldehyde	$(1.2 \pm 0.2) \times 10^{-10}$	This work	$(2.7 \pm 0.2) \times 10^{-11}$	This work	$(22 \pm 3) \times 10^{-15}$	This work
			$(2.1 \pm 0.6) \times 10^{-11}$	29	$(22.9 \pm 0.9) \times 10^{-15}$	34
			$(0.9 \pm 0.1) \times 10^{-11}$	41 <sup>d</sup>		
			$(3.06 \pm 0.44) \times 10^{-11}$	42		
Pentanal	—	—	$(2.6 \pm 0.4) \times 10^{-11}$	29	$(14.6 \pm 0.9) \times 10^{-15}$	34

<sup>a</sup> Recalculated with  $k_{\text{ethene}} = 2.1 \times 10^{-16}$  (ref. 52). <sup>b</sup> Recalculated with  $k_{\text{propene}} = 2.9 \times 10^{-11}$  (ref. 26). <sup>c</sup> Recalculated with  $k_{\text{propene}} = 9.4 \times 10^{-15}$  (ref. 27). <sup>d</sup> Recalculated with  $k_{\text{acetaldehyde}} = 1.6 \times 10^{-11}$  (ref. 52).

been made by introducing the concept of neighboring group correction factors.<sup>47,48</sup> Group rate coefficients for hydrogen atom abstraction by  $\text{NO}_3$  radical from  $-\text{CH}_3$ ,  $-\text{CH}_2-$  and  $>\text{CH}-$  have been proposed.<sup>49</sup>

In the following we attempt a qualitative discussion of how the reactive elements, *i.e.* aldehydic hydrogen atom with the associated carbonyl group, other hydrogen atoms and double bonds, affect the reactivity of the aldehydes. For the purpose of comparison, Table 1 also lists some “model” compounds that contain only one of the reactive elements. Thus, acrolein is associated with propene and propanal, crotonaldehyde with *trans*-but-2-ene, 2-methylpropanal and butanal, and pivalaldehyde with 2,2-dimethylpropane and pentanal.

**Chlorine atoms.** As is apparent from Table 2, the difference is small between rate coefficients for chlorine atom reaction with compounds where only aliphatic H-atom abstraction can take place, where also aldehydic H-atom abstraction may occur, and where addition to a double bond may contribute. In fact, some of the rate coefficients are close to the gas kinetic limited value from gas collision theory. This means that the reaction probability is high regardless of collision site and that chemical structure plays a limited role in determining the reaction rate coefficient. Nevertheless, for both unsaturated aldehydes, the rate coefficient is identical, within the limits of error, with the corresponding “model” alkene while the coefficient for the “model” aliphatic aldehyde is significantly smaller. This means that the double bond is the more important reactive element, compared with the sum of the abstractable hydrogens. Although not statistically significant, it may be noted, with reference to the discussion concerning OH and  $\text{NO}_3$  radicals below, that the rate coefficient for the unsaturated aldehyde falls below that of the alkene in both cases. This is an indication that the carbonyl group reduces the reactivity of the double bond and offsets the reactivity increase expected from the loosely bonded aldehydic hydrogen atom. Pivalaldehyde has the same rate coefficient as 2,2-dimethylpropane reacting with chlorine atoms. This shows that the aldehydic hydrogen atom adds little in terms of reactivity when the reaction probability for aliphatic hydrogen atoms is high.

**OH radical.** The rate coefficients for OH radical reactions are typically one order of magnitude smaller than the analogous Cl rate coefficients, indicating a corresponding decrease in reaction probability for the OH radical. The values for acrolein and crotonaldehyde again fall between the values for their alkene and saturated aldehyde model compounds and the differences are now large enough to be significant (*cf.* Table 1). Contrary to the corresponding Cl-atom reactions, the OH values for acrolein and crotonaldehyde are closer/identical, within the limits of error, to the saturated aldehyde model compounds. For saturated aldehydes, increase in reactivity towards OH due to “aldehydic abstraction” is obvious for pivalaldehyde and pentanal compared with pentane. Calculations using the SAR approach<sup>48</sup> show a reasonable agreement with measured results; the calculations are overestimating the rate coefficients for the unsaturated aldehydes while they underestimate the coefficient for the saturated aldehyde. The ratios  $k_{\text{calculated}}/k_{\text{measured}}$  for acrolein, crotonaldehyde and pivalaldehyde are 1.8, 1.4 and 0.5, respectively.

**$\text{NO}_3$  radical.** The rate coefficients for the reaction of  $\text{NO}_3$  radicals with the studied aldehydes are around four orders of magnitude smaller than the OH coefficients. This small probability of reaction on collision makes the coefficients very sensitive to the molecular structure, in particular to the availability of, and substitution pattern around, the double bonds. Consequently, nitrate radical rate coefficients span a much wider range than do OH- and Cl-coefficients as can be seen in Table 2. A first approach to setting up a structure–reactivity relation for unsaturated aldehydes would be to assume that the contribution from each reactive element is additive. This is apparently not true for the Cl and OH reactions where the reactivity of the unsaturated aldehyde falls between the model alkene and aldehyde. The reactivity pattern is further changed in the  $\text{NO}_3$  case where the reactivity of the unsaturated aldehydes falls well below that of both model compounds. Thus, the combination of an aldehyde functional group and a double bond lowers the reactivity of both groups towards the nitrate radical. It is possible to understand qualitatively how the double bond reactivity may be lowered by the electron-withdrawing carbonyl group. The

**Table 2** Data for Fig. 5. Rate coefficients are in  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K and 1 atm

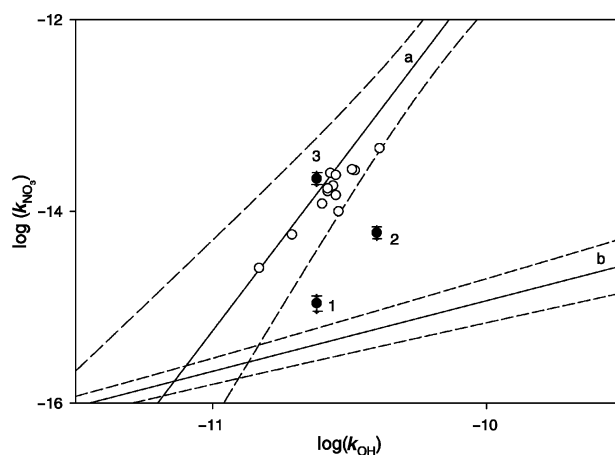
Organic compound	$k_{\text{Cl}}$	Ref.	$k_{\text{OH}}$	Ref.	$k_{\text{NO}_3}$	Ref.
<i>Alkanes—</i>						
Methane	$10.0 \times 10^{-14}$	50	$6.4 \times 10^{-15}$	51	$< 1 \times 10^{-18}$	52
Ethane	$5.75 \times 10^{-11}$	44	$2.59 \times 10^{-13}$	53	$< 1 \times 10^{-17}$	52
Propane	$1.4 \times 10^{-10}$	44	$1.09 \times 10^{-12}$	53	$< 7 \times 10^{-17}$	52
Butane	$2.15 \times 10^{-10}$	44	$2.43 \times 10^{-12}$	53	$4.5 \times 10^{-15}$	54
Pentane	$2.48 \times 10^{-10}$	45	$3.98 \times 10^{-12}$	53	$8.7 \times 10^{-17}$	55
Hexane	$2.99 \times 10^{-10}$	45	$5.45 \times 10^{-12}$	53	$1.1 \times 10^{-16}$	55
Heptane	$3.36 \times 10^{-10}$	45	$7.02 \times 10^{-12}$	55	$1.5 \times 10^{-16}$	55
Octane	$4.05 \times 10^{-10}$	45	$8.71 \times 10^{-12}$	55	$1.9 \times 10^{-16}$	55
Nonane	$4.29 \times 10^{-10}$	45	$10 \times 10^{-12}$	55	$2.3 \times 10^{-16}$	55
2-Methylpropane	$1.35 \times 10^{-10}$	45	$2.19 \times 10^{-12}$	55	$1.06 \times 10^{-16}$	55
2-Methylbutane	$2.00 \times 10^{-10}$	45	$3.70 \times 10^{-12}$	55	$1.62 \times 10^{-16}$	55
2,3-Dimethylbutane	$2.04 \times 10^{-10}$	45	$5.78 \times 10^{-12}$	55	$4.4 \times 10^{-16}$	55
<i>Alkenes—</i>						
Ethene	$1.1 \times 10^{-10}$	52	$7.9 \times 10^{-12}$	52	$2.2 \times 10^{-16}$	52
But-1-ene	—	—	$3.14 \times 10^{-11}$	55	$1.35 \times 10^{-14}$	55
2-Methylpropene	—	—	$5.14 \times 10^{-11}$	55	$3.32 \times 10^{-13}$	55
cis-But-2-ene	—	—	$5.64 \times 10^{-11}$	55	$3.50 \times 10^{-13}$	55
2-Methylbut-2-ene	—	—	$8.69 \times 10^{-11}$	55	$9.37 \times 10^{-12}$	55
2,3-Dimethylbut-2-ene	—	—	$1.10 \times 10^{-10}$	55	$5.72 \times 10^{-11}$	55
Buta-1,3-diene	$4.2 \times 10^{-10}$	56	$6.66 \times 10^{-11}$	55	$1.0 \times 10^{-13}$	55
Isoprene	$5.1 \times 10^{-10}$	57	$1.01 \times 10^{-10}$	55	$6.78 \times 10^{-13}$	55
2,3-Dimethylbuta-1,3-diene	—	—	$1.22 \times 10^{-10}$	55	$2.1 \times 10^{-12}$	55
$\alpha$ -Pinene	$4.6 \times 10^{-10}$	57	$5.37 \times 10^{-11}$	55	$6.16 \times 10^{-12}$	55
$\beta$ -Pinene	$5.3 \times 10^{-10}$	57	$7.89 \times 10^{-11}$	55	$2.51 \times 10^{-12}$	55
$\Delta^3$ -Carene	$5.6 \times 10^{-10}$	57	$8.8 \times 10^{-11}$	55	$9.1 \times 10^{-12}$	55
D-Limonene	$6.4 \times 10^{-10}$	57	$1.71 \times 10^{-10}$	55	$1.22 \times 10^{-11}$	55
Myrcene	$6.6 \times 10^{-10}$	57	$2.15 \times 10^{-10}$	55	$1.1 \times 10^{-11}$	55
<i>Aldehydes—</i>						
Acetaldehyde	$7.8 \times 10^{-11}$	58	$1.6 \times 10^{-11}$	52	$2.6 \times 10^{-15}$	59
Pentanal	—	—	$2.61 \times 10^{-11}$	59	$1.64 \times 10^{-14}$	59
Hexanal	—	—	$2.83 \times 10^{-11}$	59	$1.49 \times 10^{-14}$	59
2-Methylbutanal	—	—	$3.32 \times 10^{-11}$	59	$2.68 \times 10^{-14}$	59
3-Methylbutanal	—	—	$2.78 \times 10^{-11}$	59	$1.87 \times 10^{-14}$	59
3,3-Dimethylbutanal	—	—	$2.72 \times 10^{-11}$	59	$2.49 \times 10^{-14}$	59
2-Methylpentanal	—	—	$3.22 \times 10^{-11}$	59	$2.73 \times 10^{-14}$	59
3-Methylpentanal	—	—	$2.84 \times 10^{-11}$	59	$2.41 \times 10^{-14}$	59
4-Methylpentanal	—	—	$2.61 \times 10^{-11}$	59	$1.73 \times 10^{-14}$	59
2-Ethylbutanal	—	—	$4.12 \times 10^{-11}$	59	$4.61 \times 10^{-14}$	59

reactivity reduction of the aldehydic hydrogen atom however is somewhat surprising and there is no obvious explanation for this phenomenon. One possibility is that the conjugated  $\pi$ -system, created by the C=C double bond and carbonyl C=O double bond, increases the rotation barrier of the aldehyde CHO group, thereby reducing the availability of the aldehydic hydrogen atom.

### Linear correlations

An excellent but more information-demanding way of predicting rate coefficients, compared with the addition of group reactivities, is to use so-called linear free energy relations. Provided that the primary reaction mechanism (*i.e.* abstraction or addition) is the same for both the OH and  $\text{NO}_3$  radicals, a linear relation exists between  $\log(k_{\text{NO}_3})$  and  $\log(k_{\text{OH}})$  for the same organic reactant. By plotting a number of such pairs, a straight line is obtained that can be used to calculate one rate coefficient for a compound if the other constant is already known. Such diagrams may also be used to distinguish between reaction mechanisms for a reaction by observing on which line a pair of data falls. This is illustrated by Fig. 5. By using such linear free energy diagrams, evidence has been presented for saturated aldehydes reacting with nitrate radicals by an addition–elimination mechanism<sup>34</sup> although the apparent mechanism would be a direct abstraction of the aldehydic hydrogen atom. The addition/adduct formation obviously plays a role in the aldehyde– $\text{NO}_3$  reaction and the adduct concentration would control the reaction rate. Aliphatic aldehydes, and also pivalaldehyde, fit remarkably well on the

“addition” line as shown in Fig. 5. Acrolein and crotonaldehyde, on the other hand, fall in the area between addition and abstraction lines. This could indicate that these reactions proceed both *via* addition to the double bond or the aldehydic hydrogen, and by abstraction of aliphatic hydrogen atoms. It



**Fig. 5** Linear free energy plot of  $\log(k_{\text{NO}_3})$  vs.  $\log(k_{\text{OH}})$ . a, Regression line for 16 addition reactions; b, regression line for 12 abstraction reactions. Open circles represent 13 aliphatic aldehydes. Closed circles with the error bars represent results from this study. 1, Acrolein; 2, crotonaldehyde and 3, pivalaldehyde. The broken lines represent the 95% confidence intervals for the addition and abstraction lines. References are found in Tables 1 and 2.

should be noted that the error bars should be taken into consideration in this interpretation. However, according to the literature, the primary reaction mechanism for nitrate radical reaction with acrolein is believed to be mainly abstraction of the aldehydic hydrogen atom, while for crotonaldehyde, the reaction proceeds *via* both pathways.<sup>30,60</sup> In this case, it seems that the adduct/elimination path is not operating for the unsaturated aldehydes, and that an ordinary abstraction of the aldehyde hydrogen atom takes place.

## Conclusions

The reaction probability of chlorine atoms with organic compounds is high and the chemical structure plays a limited role in the magnitude of the rate coefficient. Chlorine atoms are daytime species since they are formed by photolysis of chlorine-containing substances accumulated in the atmosphere during the dark hours. As such, they compete with hydroxyl radicals *e.g.* for organic compounds. Peak concentrations of chlorine atoms as high as  $10^4$ – $10^5$  cm<sup>-3</sup> have been predicted in coastal areas during early sunrise.<sup>61</sup> Hydroxyl radical concentrations during the same time period have been measured to be between 1 and  $5 \times 10^5$  cm<sup>-3</sup>.<sup>62</sup> Taking into account that Cl rate coefficients are often a factor of ten higher than the corresponding OH rate coefficients, then it appears that, at least for a short period during the morning hours, Cl atoms may be the most significant oxidizing agent for organic substances in urban coastal air.

Differences in rate coefficients for the OH initiated reactions with various organic compounds are still small but large enough to give useful trends caused by molecular structure. Calculations of rate coefficients made with the SAR approach, with respect to the aldehydes investigated, gave results within a factor of two compared with measured values. For NO<sub>3</sub> initiated reactions, the span of rate coefficient values is large due to the much higher selectivity of the radical, and the molecular structure of the reacting organic compound is very important. Aldehydic carbonyl groups appear to decrease the reactivity of neighboring double bonds in all cases. For the nitrate radical reaction with unsaturated aldehydes, the double bond, in turn, appears also to decrease the reactivity of the aldehydic hydrogen atom. This influence on reactivity by functional groups for NO<sub>3</sub> and unsaturated aldehydes is somewhat unexpected. Pivalaldehyde most probably reacts in a way common for saturated aldehydes, addition followed by elimination.<sup>34</sup> The linear free energy relation between NO<sub>3</sub> and OH rate coefficients indicates that the reaction mechanism for acrolein and crotonaldehyde is a mixture of addition and abstraction. For acrolein and crotonaldehyde, the detailed reaction mechanism cannot be determined only from kinetic consideration.

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