

Reactivity of 2-ethyl-1-hexanol in the atmosphere

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Rate coefficients at room temperature for the reaction of 2-ethyl-1-hexanol with OH and NO₃ radicals and with Cl atoms have been determined in a 150 L PTFE chamber using GC-FID/SPME and FTIR as detection systems. The rate coefficients *k* (in units of cm³ molecule⁻¹ s⁻¹) obtained were: (1.13 ± 0.31) 10⁻¹¹ for the OH reaction, (2.93 ± 0.92) 10⁻¹⁵ for the NO₃ reaction and (1.88 ± 0.25) 10⁻¹⁰ for the Cl reaction. Despite the high concentrations of 2-ethyl-1-hexanol, especially in indoor air, this is the first kinetic study carried out to date for these reactions. The results are consistent with the expected reactivity given the chemical structure of 2-ethyl-1-hexanol. Calculated atmospheric lifetimes reveal that the dominant loss process for 2-ethyl-1-hexanol is clearly the daytime reaction with the hydroxyl radical.

Introduction

2-Ethyl-1-hexanol is an organic compound that is detected in indoor air at relatively high concentrations (above 400 µg m⁻³).¹ This compound is considered to be a pollutant, is one of the causes of odour in indoor air and is implicated in sick building syndrome.^{1,2} It is primarily emitted from flooring made from polyvinyl chloride (PVC) building materials, which include di-2-ethylhexylphthalate (DEPH) as a plasticizer.³ DEPH is hydrolyzed under alkaline conditions arising from slabs and self-leveling sub-flooring materials that contain cement, and as a consequence, 2-ethyl-1-hexanol is emitted from floors that are water damaged or contain insufficient dried cement-based flooring substrate.

2-Ethyl-1-hexanol is also considered to be a microbial volatile organic compound (MVOC), and is produced along with other volatile organic compounds in the decomposition of complex organic material. Irritations of the eyes and mucous membranes as well as several non-specific symptoms and discomfort, are often attributed to the presence of MVOCs.⁴ For several years there has been a continued interest in finding typical indicator components within the range of characteristic MVOCs originating from indoor mould. A number of compounds have already been proposed as indicators of mould⁵ and 2-ethyl-1-hexanol can also be used as an indicator of mould growth and in mould exposed dwellings.

Finally, it is important to mention that 2-ethyl-1-hexanol could also be a significant pollutant in outdoor air as it has been identified as one of the top 20 chemicals in concentration produced for biodiesel vapors.⁶ Considering that many countries

are encouraging the use of biodiesels, evaporative emissions of compounds like this must be considered.

Once this compound has been released into the atmosphere, as other VOCs, it will react with atmospheric oxidants mainly with OH and NO₃ radicals.

In spite of the high concentrations of this compound detected, experimental studies have not been carried out on the reactivity of this compound with the OH radical (main oxidant at daytime), the NO₃ radical (main oxidant at night time), ozone molecules and Cl atoms. Such studies are essential to determine the lifetime and persistence of this compound in the atmosphere, and therefore to evaluate the consequences of its presence on health and the environment.

We describe here the first determination of rate coefficients at room temperature for the reactions of 2-ethyl-1-hexanol with the OH and NO₃ radicals and with Cl atoms. The experiments were carried out in a 150 L PTFE chamber using the relative technique combined with solid-phase microextraction (SPME) sampling and gas chromatography with flame ionization detector (GC-FID) as the analysis system. FTIR spectroscopy was used to complete the results for OH reactions as explained below. Lifetimes corresponding to each of the reactions in question were also calculated and the implications for the atmosphere are discussed.

Experimental

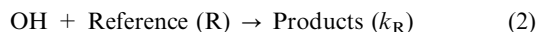
Equipment, chemicals and method

Experiments were performed in a 150 L FEP Teflon reaction bag at a total pressure of (708 ± 8) Torr (synthetic air or N₂). The bag was placed inside a rectangular cage with 4 fluorescent lamps (Philips TUV G13 36W) mounted on the walls. A detailed description of the experimental system can be found elsewhere.^{7,8} Briefly, rate coefficients for the reaction of 2-ethyl-1-hexanol with OH and NO₃ radicals and with Cl atoms at 298 ± 2 K were determined using a relative rate method. In this technique the disappearance of the substrate

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2-ethyl-1-hexanol due to reaction with the reactive species (OH, NO₃ or Cl) is measured relative to that of a reference compound, the rate coefficient of which with the reactive species is reliably known, *e.g.*,



As described in detail elsewhere,⁹ the decay of the substrate from [S]₀ at time *t* = 0 to [S]_{*t*} at time *t*, and the simultaneous loss of the reference compound from an initial concentration of [R]₀ to [R]_{*t*} at time *t* is given by eqn (I):

$$\ln\left(\frac{[\text{S}]_0}{[\text{S}]_t}\right) = \frac{k_{\text{S}}}{k_{\text{R}}} \ln\left(\frac{[\text{R}]_0}{[\text{R}]_t}\right) \quad (\text{I})$$

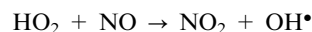
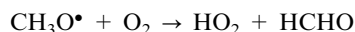
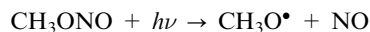
Thus, a plot of {ln[S]₀/[S]_{*t*}} versus {ln[R]₀/[R]_{*t*}} should be a straight line passing through the origin and the slope gives the ratio of rate coefficients *k*_S/*k*_R. At each sampling the ratio of concentration of the reference or substrate against the concentration of an internal standard was used in rate coefficient calculations. The internal standard was benzene due to the low rate coefficients with OH, NO₃ and Cl.^{10–12} The use of this method allowed us to minimize the sampling errors. Each reaction studied was measured relative to the reaction of two reference standards. The decay of the reactant, reference compound and internal standard were monitored by gas chromatography with flame ionization detection (GC-FID, Shimadzu 14A) using a capillary column (30 m × 0.32 mm × 1 μm, TRACSIL TRB-1701, TEKNOKROMA) of intermediate polarity. Prior to the experiments, a run was performed in scanning mode to determine the retention time of each reactant. Additional sets of runs were also carried out with each individual reference compound or with the alcohol to ensure that the reactions did not produce products with retention times that could interfere with the reactant peaks used in the kinetic analysis. Additionally, all organics were subjected to radiation alone to ensure that photolysis was negligible in all cases and to confirm that unrecognized reactions did not occur in the absence of OH, NO₃ or chlorine atom sources. To test for dark reactions, the precursor of the radical and the organics were kept in the reactor for a certain period of time (≈8 h) in the absence of photolysis and no significant variation of the chromatographic areas was obtained. The occurrence of secondary chemistry was ruled out on the basis of experiments with different concentrations of the reference and the alcohol which showed consistency in the slopes in all cases (with intercepts at zero). Finally, for each organics mixture a number of injections (typically 12 or more) of the unreacted mixture was carried out to obtain an estimate of the precision associated with the measurements for use in error analysis.¹³ The reproducibility of these measurements also included losses due to the walls of the reaction bag, and it was found that wall losses were not significant.

Therefore, under the experimental conditions it can be considered that the areas of chromatographic peaks relative to the standard internal, for the substrate (*S*) and the reference compound (*R*), at times 0 and *t* respectively, are proportional to the concentration.

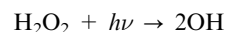
Oxidants were generated according to the following methods:

OH reactions

Methyl nitrite (CH₃ONO) previously generated in the laboratory as described elsewhere¹⁴ was used in the presence of air and NO to generate OH radicals through photolysis according to the following reactions:



UV radiation with a maximum at around 360 nm was supplied by appropriate lamps. H₂O₂ was also used as an alternative source of OH radicals by direct UV photolysis with germicidal lamps emitting at 254 nm surrounding the Teflon bag, according to the following reaction:



In this case, N₂ was used as carrier gas.

NO₃ reactions

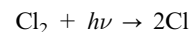
NO₃ radicals were produced by the thermal decomposition of N₂O₅ according to the reaction:



N₂O₅ was synthesized according to the method described by Schott and Davidson.¹⁵ Experiments were performed with N₂ as carrier gas.

Cl reactions

Photolysis at 360 nm of molecular chlorine (Cl₂) was used to generate atomic chlorine.



Experiments were performed with N₂ as carrier gas.

Photolysis was typically carried out in steps of 30–120 s, after which the lamps were turned off and the reaction mixture was sampled.

The experimental procedure was as follows: the carrier gas was N₂ or air, then 2-ethyl-1-hexanol, the reference compound, the standard compound and the precursor of the oxidant were introduced into the reactor.

The initial concentrations employed in the experiments are summarized in Table 1. Several runs were performed for the rate constant determination. Concentrations of the substrate and the reference compounds were monitored by means of gas chromatography with flame ionization detection, as explained above. The routine method to introduce the sample into the analytical system (a chromatograph) involved transferring the reaction mixture from the reactor to the injection valve (loop) of the chromatograph by means of a pump. In the case of 2-ethyl-1-hexanol it was necessary to modify the injection method due to condensation of this compound in the transfer

Table 1 Reactant concentrations (in units ppm) employed in the experiments

Reaction	[Substrate]	[Reference]	[Precursor]
2-Ethyl-1-hexanol + Cl	0.74–1.98	1.48–2.97	24–200
2-Ethyl-1-hexanol + NO ₃ •	0.74–1.98	4.95–14.85	5.94–19.80
2-Ethyl-1-hexanol + OH•	0.74–1.98	2.13–9.90	NO CH ₃ NO ₂ 5–50 30–95

line. As a result, solid phase microextraction (SPME) was used as the sampling method.

The thermodynamic aspects of this technique have been studied extensively and it was shown that the amount of sample extracted by the fiber is directly proportional to the concentration of the sample in the reactor.¹⁶ Solid phase microextraction was developed by Arthur and Pawliszyn.¹⁷ The application of SPME in the study of atmospheric reactivity has two uses: firstly, as a preconcentration method during identification of the reaction products^{18–21} and secondly, to a lesser extent as a tool for sampling during the kinetic study of certain reactions.^{22–26} The reaction sample was collected from the reactor by inserting the fiber (polymer mixture of divinylbenzene, carboxen and poly(dimethylsiloxane) (DVB/CAR/PDMS), 50/30 µm SPME, SUPELCO) in the reactor, through a septum positioned at its centre. After optimization of the time, the fiber was exposed to the gas mixture for 15 min. After sampling, the fiber was inserted into the GC injector for thermal desorption (during 10 min at 270 °C) followed by chromatographic separation. The fiber was used after desorption for the next sampling.

Additionally, as mentioned above, prior to the determination of rate coefficients, several experiments were carried out in order to ensure the absence of dark and heterogeneous reactions in the typical time span of the kinetic experiment and to confirm that secondary chemistry and photolytic loss of the compounds studied were negligible.

For OH and Cl reactions, the total photolysis times and conversion of reactant are presented in Table 2. In the case of NO₃ reactions, N₂O₅ was introduced in incremental amounts in the reactor, and conversion of reactants in this case is also included in Table 2.

Chemicals used in this study and their sources and purities were as follows: N₂ (Praxair, Ultrahigh Purity, 99.999%) purified using an Oxisorb trap and a molecular-sieve trap, Synthetic air (99.999% Praxair), Cl₂ (Praxair, ≥ 99%), Organics: 2-ethyl-1-hexanol, (99%), cyclohexane (≥ 99%), n-nonane (99%), n-heptane (≥ 99), furan (≥ 99%), octanol (99%), methacrolein (95%) were obtained from Aldrich Chemical Co. and were purified by successive trap-to-trap distillations.

Table 2 Total photolysis times and conversion of reactants

Reaction	<i>t</i> _{photolysis} /s	% Conversion	
		Substrate	Reference
2-Ethyl-1-hexanol + Cl	45–390	30–67	33–73
2-Ethyl-1-hexanol + OH•	120–710	18–64	25–71
2-Ethyl-1-hexanol + NO ₃ •	—	26–61	33–60

Results

As indicated above, dark and heterogeneous reactions were not observed and photolytic loss of the compounds studied was calculated to be negligible. Rate coefficients for the reactions of the reference compounds (*k_R*) employed in this work are presented in Table 3. The use of the technique described above allowed the rate constant of the studied reaction to be obtained from eqn (I).

Data were fitted to a straight line by the linear least squares procedure. The ratio *k_S/k_R* was obtained using a linear regression that takes into account errors in both the abscissa and the ordinate.¹³ The total absolute error Δ*k_S* of rate coefficients included both the 95% confidence limits from the slopes and the quoted error in the value of the rate coefficient for the reference compound. The second-order rate coefficients for the reference compounds used *k_R*, are accurately known, thus allowing *k_S* to be determined.

The rate coefficients determined in this work for the reactions of OH, NO₃ radicals and Cl atoms with 2-ethyl-1-hexanol are summarized in Table 4.

It can be seen from the results that the reference compounds employed for the different studied reactions are also different. The reference compounds were selected according to the following criteria: well determined rate coefficient; a chromatographic peak that does not interfere with other peaks; and a rate coefficient of the same order as that to be determined. Good reproducibility of the results is also essential. Several compounds were identified that meet these criteria for OH and Cl reactions. Nevertheless, in the case of NO₃ reactions, we tested several reference compounds whose results were not reproducible using the SPME-FID technique. Therefore, we decided to use butanol—the rate coefficient of which had been determined in our laboratory and was consistent with the conditions as a good reference compound.

OH reactions

The reaction of OH radical with 2-ethyl-1-hexanol was studied relative to the reactions of cyclohexane and octanol with this oxidant. A plot of the relative data for the reaction of OH (OH generated using methyl nitrite) with 2-ethyl-1-hexanol with the two reference compounds used in this case is shown in Fig. 1. Ar(*S*₀), Ar(*R*₀), Ar(*S*_{*t*}) and Ar(*R*_{*t*}) are the areas of the chromatographic peaks relative to the standard internal for the substrate (*S*) and the reference compound (*R*), at times 0 and *t* respectively, and that are proportional to concentrations.

Table 3 Rate coefficients (*k* in units of cm³ molecule^{−1} s^{−1}) for the reaction of OH and NO₃ radicals and Cl atoms with the reference compounds used in this work. (Bibliographic references also presented in the table)

Compound	<i>k_r</i>	Reference
Cyclohexane	<i>k</i> _{OH} = (6.97 ± 0.70) × 10 ^{−12} <i>k</i> _{Cl} = (3.07 ± 0.34) × 10 ^{−10}	Atkinson, 2003 ⁴² Aschmann, 1995 ⁴³
Ethene	<i>k</i> _{OH} = 8.51 × 10 ^{−12}	Atkinson 1990 ⁴⁴
Furan	<i>k</i> _{Cl} = (2 ± 0.2) × 10 ^{−10}	Cabañas 2005 ⁷
Methacrolein	<i>k</i> _{NO₃} = (3.30 ± 1) × 10 ^{−15}	Chew 1998 ²⁷
Octanol	<i>k</i> _{OH} = (1.44 ± 0.14) × 10 ^{−11}	Nelson, 1990 ²⁹
Propene	<i>k</i> _{OH} = 2.63 × 10 ^{−11}	Atkinson 1990 ⁴⁴

Table 4 Relative and absolute rate coefficients (k in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for the reaction of 2-ethyl-1-hexanol with OH and NO_3 radicals and Cl atoms, and for the reaction of n-butanol with NO_3 radical

Reaction	Reference compound	$\frac{k_s}{k_R}(\pm 2\sigma)$	$k_s (\pm 2\sigma)$
2-Ethyl-1-hexanol + OH (CH_3ONO as precursor)	Cyclohexane	1.203 ± 0.04	$(0.84 \pm 0.30) \times 10^{-11}$
	Octanol	0.952 ± 0.03	$(1.37 \pm 0.14) \times 10^{-11}$
2-Ethyl-1-hexanol + OH (H_2O_2 as precursor)	Cyclohexane	1.621 ± 0.044	$(1.13 \pm 0.12) \times 10^{-11}$
	Octanol	0.645 ± 0.0	$(0.93 \pm 0.09) \times 10^{-11}$
2-Ethyl-1-hexanol + OH (CH_3ONO as precursor and FTIR)	Propene	0.474 ± 0.008	$(1.22 \pm 0.02) \times 10^{-11}$
	Ethene	1.457 ± 0.031	$(1.24 \pm 0.08) \times 10^{-11}$
n-Butanol + NO_3	Methacrolein	0.950 ± 0.41	$(3.14 \pm 0.97) \times 10^{-15}$
2-Ethyl-1-hexanol + NO_3	Butanol	0.940 ± 0.04	$(2.95 \pm 0.92) \times 10^{-15}$
	Methacrolein	0.926 ± 0.06	$(2.91 \pm 0.92) \times 10^{-15}$
2-Ethyl-1-hexanol + Cl	Cyclohexane	0.633 ± 0.03	$(1.94 \pm 0.28) \times 10^{-10}$
	Furan	0.911 ± 0.06	$(1.82 \pm 0.22) \times 10^{-10}$

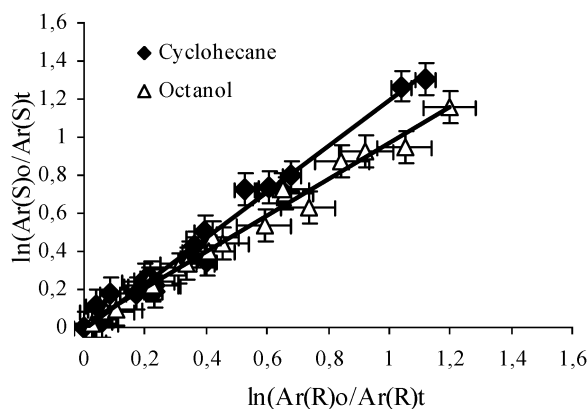


Fig. 1 Relative rate plots for OH + 2-ethyl-1-hexanol with two reference compounds (CH_3ONO as precursor for OH radicals).

On using CH_3ONO as the precursor for OH radicals, discrepancies in rate coefficients determined with the two reference compounds are observed, as can be seen in Table 4. These differences could arise because NO (necessary for the OH generation) poisons the fiber and this affects the results. For this reason, H_2O_2 was also used as a precursor for OH generation, and a plot of the experimental data plotted in this case is shown in Fig. 2.

Additional experiments on reactions with OH generated using CH_3ONO as the precursor were carried out in a glass

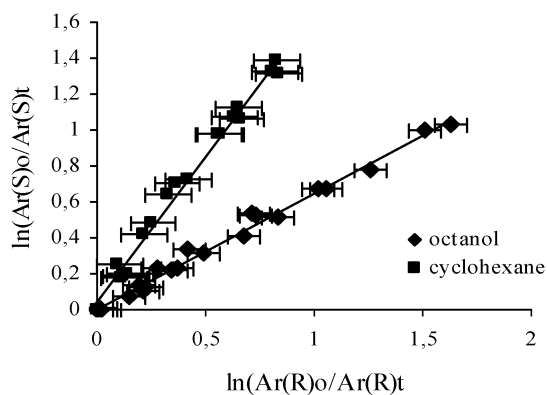


Fig. 2 Relative rate plots for OH + 2-ethyl-1-hexanol with two reference compounds (H_2O_2 as the precursor for OH radicals).

reactor with long-path FTIR spectroscopy used to monitor the reaction. Briefly, the reaction chamber is a cylindrical quartz-glass reactor at atmospheric pressure and room temperature with a volume of 50 L.

The reactor is equipped with a White mirror system with a base optical path of 1.5 m. and a maximum total path length of 200 m. Fourier transform infrared spectroscopy (Thermo Nicolet 5700 spectrometer with an MCT detector cooled by liquid nitrogen) was used to follow the reaction of 2-ethyl-1-hexanol and the reference compound with OH radicals generated *in situ* as explained above. Propene and ethene were used as reference compounds in this case. Spectral subtraction was used to ascertain the relative concentrations of the reactants at different time intervals during the reactions. The relative rate coefficients were determined according to eqn (I). Relative plots with the two reference compounds are shown in Fig. 3 for the mentioned reaction.

The errors quoted are combination of the 2σ statistical errors from the regression analysis together with the errors from the spectral subtraction procedure.

NO_3 reaction

In this case, n-butanol and methacrolein were selected as reference compounds. Then rate coefficient of butanol was also determined in our laboratory because the value previously reported was a

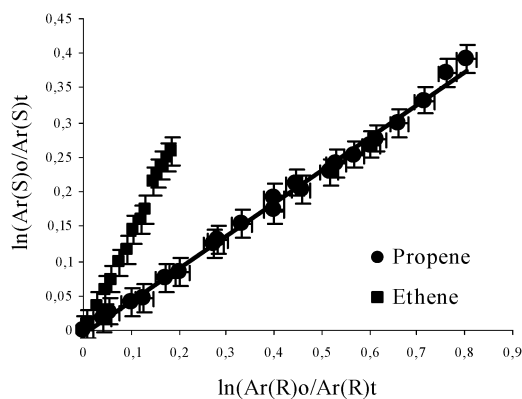


Fig. 3 Relative rate plots for OH + 2-ethyl-1-hexanol with two reference compounds obtained using FTIR spectroscopy (CH_3ONO as precursor for OH radicals).

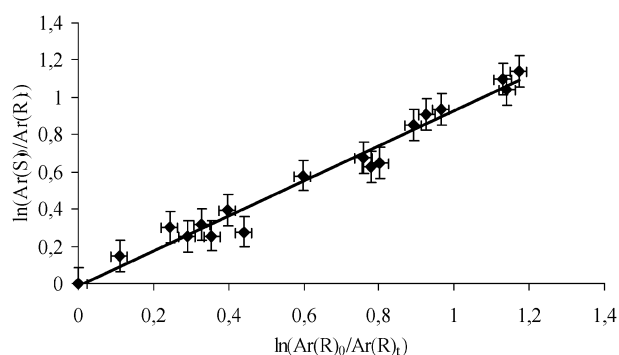


Fig. 4 Relative rate plots obtained for 2-ethyl-1-hexanol with NO_3 radical using n-butanol as the reference compound.

higher limit ($< 2.71 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).²⁷ Methacrolein was used as the reference compound in this case, and the calculated coefficient for butanol is also included in Table 4. Once second order rate constant of n-butanol was accurately determined, we used this compound as reference. The relative rate plots for the reaction of NO_3 radicals with 2-ethyl-1-hexanol using n-butanol and methacrolein as reference compounds are represented in Fig. 4 and 5, respectively.

Cl reaction

The relative rate plots for the reaction of Cl atoms with the substrate using furan and cyclohexane as reference compounds are shown in Fig. 6.

Discussion

As can be seen from Fig. 1–6, and in agreement with eqn (I), the data give straight lines that pass through the origin (within experimental error) with a slope of k_S/k_R , indicating that secondary reactions or heterogeneous processes are insignificant.

It can be seen from the results in Table 4 that there is a good agreement between the values of k determined using two different reference compounds. The exception to this is the case of OH reactions with SPME-FID technique using CH_3ONO as the precursor for OH, as mentioned above. The values for

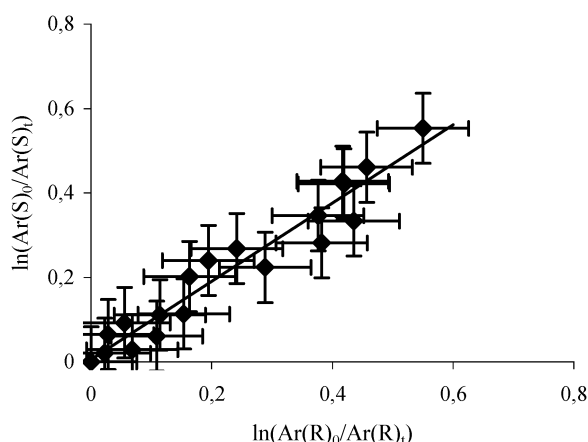


Fig. 5 Relative plot for 2-ethyl-1-hexanol reaction with NO_3 radical using methacrolein as the reference compound.

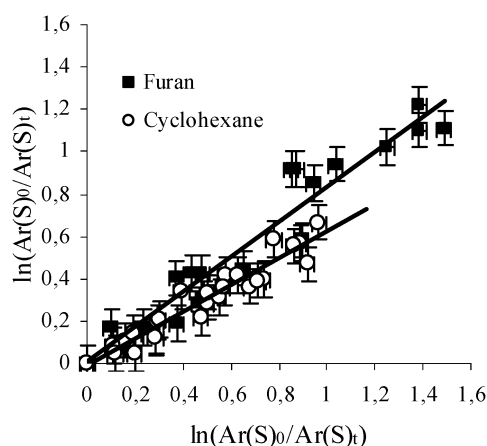


Fig. 6 Relative rate plots for 2-ethyl-1-hexanol reaction with Cl atoms using two reference compounds.

this case are included in the Table, but were omitted in the rate coefficient determination.

It can be concluded that CH_3ONO cannot be used as precursor when this technique is used as the detection method. Rate coefficients obtained using H_2O_2 (with SPME-FID detection) or methylnitrite (with FTIR detection) as precursors for OH radicals are the same, within the experimental errors, and it can be therefore concluded that these coefficient have been accurately determined.

The rate coefficients obtained in this work for 2-ethyl-1-hexanol reactions with OH and NO_3 radicals, and with Cl atoms after calculating the average values are summarized in Table 5. Comparison of the reactivity of the three oxidants shows that the rate coefficient for the reaction involving Cl atom is about one order of magnitude higher than that for the OH reaction and five orders of magnitude higher than that for the NO_3 reaction.

The discrepancies initially observed for OH reactions led us to compare the result of this rate coefficient with estimations obtained using a structure activity relationship (SAR) algorithm by Atkinson and Kwok.²⁸ Briefly, the calculation of H-atom abstraction rate constants from C–H and O–H bonds is based on the estimation of group rate constants for H-atom abstraction from $-\text{CH}_3$, $-\text{CH}_2-$, $>\text{CH}-$ and $-\text{OH}$ groups. The rate constants for H-atom abstraction depend on the nature of the substituents attached to these groups, with

$$k(\text{CH}_3-\text{X}) = k_{\text{prim}}F(\text{X})$$

$$k(\text{X}-\text{CH}_2-\text{Y}) = k_{\text{sec}}F(\text{X})F(\text{Y})$$

$$k(\text{X}-\text{CH}(\text{Y})(\text{Z})) = k_{\text{terc}}F(\text{X})F(\text{Y})F(\text{Z})$$

$$k(\text{H}-\text{O}-\text{C}(\text{X})(\text{Y})) = k_{\text{alc}}F(\text{X})F(\text{Y})F(\text{Z})$$

where k_{prim} , k_{sec} and k_{terc} are the group rate constants for H-atom abstraction from $-\text{CH}_3$, $<\text{CH}_2-$, $>\text{CH}-$ and OH groups respectively, for a “standard” substituent, and $F(\text{X})$, $F(\text{Y})$ and $F(\text{Z})$ are the substituent factors for the substituent groups X, Y and Z, respectively. The standard substituent group is chosen to be $(\text{X} = \text{Y} = \text{Z}) = -\text{CH}_3$, with $F(-\text{CH}_3) = 1.00$ by definition. According to this, for 2-ethyl-1-hexanol, the

Table 5 Rate coefficients and atmospheric lifetimes determined for the reactions of 2-ethyl-1-hexanol with the atmospheric oxidants OH and NO₃ radicals, and Cl atoms

Reaction	$\bar{k}_S (\pm 2\sigma) / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	τ / h
2-Ethyl-1-hexanol + OH	$(1.13 \pm 0.31) \times 10^{-11}$	24.6
2-Ethyl-1-hexanol + OH SAR calculation	1.32×10^{-11}	21.0
2-Ethyl-1-hexanol + NO ₃	$(2.93 \pm 0.92) \times 10^{-15}$	189.6
2-Ethyl-1-hexanol + Cl	$(1.88 \pm 0.25) \times 10^{-10}$	147.8

global abstraction rate coefficients can be calculated as follows:

$$k_{\text{abs}} = \Sigma[k_{\text{prim}}F(X)] + \Sigma[k_{\text{sec}}F(X)F(Y)] \\ + \Sigma[k_{\text{terc}}F(X)F(Y)F(Z)] + \Sigma[k_{\text{alc}}F(X)F(Y)F(Z)]$$

Group rate constants and substituents factor employed for calculation are summarized in Tables 6 and 7 and the estimated rate coefficient for the reaction of OH with 2-ethyl-1-hexanol of $1.32 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is very similar to that determined experimentally in our work.

To the best of our knowledge, values for the reactions studied here have not been reported previously and therefore direct comparison with the literature data cannot be made. However it is interesting to compare the reactivity of 2-ethyl-1-hexanol with previously reported reactions of other alcohol with these atmospheric oxidants. Generally, these reactions occur by H-atom abstraction from both C–H and O–H bonds.

For OH reactions, rate coefficients of aliphatic alcohols are in the range of $(1\text{--}15) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and the reactivity increases with the length of the hydrocarbon chain.^{29–33} 2-Ethyl-1-hexanol has a rate coefficient of $k = 1.13 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, that is similar to the value for hexanol ($k = 1.22 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). The ethyl group in the α -position increases the reactivity due to the electron-donating inductive effect, but we believe that steric impediments could compensate for this increase, giving rate coefficients of the same order of magnitude. More data for long chain alcohols are required in order to confirm this supposition.

For the reactions of NO₃ with alcohols, rate coefficients of methanol, ethanol, propanol and butanol have previously been measured and an increase in rate coefficients with the chain length is normally observed.^{27,34} In this study we recalculated the previous value obtained for butanol and a value of $3.14 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was found. The experimental value determined in our work for 2-ethyl-1-hexanol is $3 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which again indicates that some steric impediment in the electrophilic attack of the oxidant for H-atom abstraction is compensating the increase in reactivity expected on increasing the chain length and for the presence of the ethyl group.

Table 6 Group rate constants for H-atom abstraction from –CH₃, –CH₂–, >CH– and OH groups

k (group)	$k/10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
k_{prim}	1.36
k_{sec}	9.34
k_{terc}	19.4
k_{alc}	1.40

Table 7 Substituents factors F(X) at 298 K used for calculation of the abstraction rate coefficient of OH radical reaction with 2-ethyl-1-hexanol

Substituent	F(X)
–CH ₃ –	1
–CH ₂ –	1.23
–CH–	1.23
OH	3.5

For Cl reactions, the available literature indicates that rate coefficients are in the range of $(1\text{--}3.5) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and a clear difference in reactivity is not observed as a function of the position or the length of alkyl chain.^{29,31,35} In accordance with this situation, 2-ethyl-1-hexanol has a rate coefficient in the expected range for these compounds.

The rate coefficients summarized in Table 5, can be used to calculate the atmospheric lifetimes of 2-ethyl-1-hexanol due to the reaction with the three major atmospheric oxidants, OH and NO₃ radicals and Cl atoms using the expression: $\tau_R = 1/(k_R[\text{Ox}])$ where [Ox] is the typical atmospheric concentration of OH, NO₃, and Cl respectively, and k_R is the rate coefficient of the reaction of the oxidant with the alcohol determined in this work. As indicated above, photolytic loss of the compound studied here was calculated to be negligible.

The typical tropospheric concentrations of OH, NO₃ and Cl used in the calculations were:^{36–38} $[\text{Cl}] = 1 \times 10^4 \text{ atom cm}^{-3}$, $[\text{OH}] = 1 \times 10^6 \text{ radical cm}^{-3}$, $[\text{NO}_3] = 5 \times 10^8 \text{ radical cm}^{-3}$. The atmospheric lifetimes determined with the above expression and presented in Table 5 and clearly indicate that the dominant atmospheric loss process for 2-ethyl-1-hexanol is the daytime reaction with the hydroxyl radical. This conclusion is drawn because lifetimes are in the range of hours (24 h) implying that this alcohol is likely to be removed in the gas phase close to the emission sources. Therefore, the atmospheric relevance of the degradation products of this process should also be considered when atmospheric implications are evaluated. The NO₃ and Cl degradation reactions of 2-ethyl-1-hexanol are of the order of days, implying less relevant processes. However, in coastal areas and in the marine boundary layer, where peak concentrations of Cl atoms as high as $1 \times 10^5 \text{ atoms cm}^{-3}$ can occur,³⁹ lifetimes calculated with this concentration are ten times lower (14.7 h), indicating that Cl atom-initiated degradation of this compound can be an important homogeneous loss process.

Additional atmospheric implications that can be evaluated concern the impact of ozone production derived from the presence of 2-ethyl-1-hexanol in the atmosphere. The appropriate quantification of the impact of ozone is the incremental

reactivity (IR), which is the amount of additional ozone formation, caused by adding a small amount of the compound to the emissions, divided by the amount emitted.^{40,41} Values of IR and of the maximum incremental ozone reactivities (MIRs) have been estimated the literature for volatile organic compounds (VOCs). These values are available for more than 100 VOCs with estimated rate coefficients used for the calculations. 2-Ethyl-1-hexanol is included in this classification with a MIR value of 2.54 g g^{-1} , using an estimated rate coefficient for the OH reaction of $1.33 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, a value that is consistent with that experimentally determined in this work.

Conclusions

In spite of the high concentrations detected for 2-ethyl-1-hexanol in indoor air and the relevant emission of this compound in biodiesel vapors, this is the first kinetic study carried out to date for the reactions in question. Rate coefficients at room temperature for the reactions of 2-ethyl-1-hexanol with OH and NO₃ radicals and with Cl atoms, clearly indicate that reaction with OH is the most relevant degradation process for this compound in the atmosphere. In this case an atmospheric lifetime of 24.6 h was determined, indicating that this alcohol remains in the atmosphere long enough to produce health effects, as mentioned in the Introduction. The rate coefficients determined are consistent with the expected reactivity given the chemical structure of this compound.

Notes and references

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