

The reaction of acetaldehyde and propionaldehyde with hydroxyl radicals: experimental determination of the primary H₂O yield at room temperature

Sabine Vandenberg, Jozef Peeters*

Department of Chemistry, University of Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium

Received 20 June 2002; received in revised form 20 September 2002; accepted 30 September 2002

Abstract

The branching fraction of H-abstraction in the elementary reactions of acetaldehyde and propionaldehyde with OH at 290 K was determined directly using a fast-flow reactor coupled to a molecular beam sampling mass spectrometry apparatus. The primary-product H₂O yield of the title reactions was quantified relative to that of the isobutane + OH reaction, and found to be 89 ± 6 and $100 \pm 10\%$ for the reactions of acetaldehyde + OH and propionaldehyde + OH, respectively. Furthermore, an upper limit of 3% could be determined for the yield of formic acid in the hypothetical addition/elimination reaction pathway. We conclude that the reaction of OH radicals with aldehydes proceeds predominantly, if not exclusively, via H-abstraction, forming H₂O and R-CO.

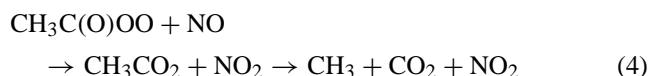
© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Acetaldehyde; Propionaldehyde; Hydroxyl radicals; H-atom abstraction; Product distribution; Troposphere

1. Introduction

Aldehydes play an important role in the photochemistry of the polluted troposphere. They are a result of direct emissions from anthropogenic or biogenic sources or are themselves intermediates in the photo-oxidation processes of most organic compounds in the troposphere [1,2]. Aside from the possible relationship of aldehydes to problems as toxicity, eye irritation and odor problems, they can provide significant photolytic sources of radicals such as HO₂, OH and RO₂ which control ozone production from CH₄ and CO in the free troposphere and influence the rate of photochemical oxidant formation under ambient conditions [3,4]. An additional role for aldehydes is as precursors to the formation of peroxyacyl nitrates, which are phytotoxic and strongly eye-irritating compounds [4]. The reaction of acetaldehyde + OH is expected to be the main source for peroxyacetyl nitrate (PAN), a reservoir compound for NO_x, which can be transported over long distances at the low temperatures of the higher troposphere and can change the NO_x levels in remote areas, leading to a different photochemical BVOC/NO_x-oxidation mechanism. Atkinson and Lloyd [5] reported the following mechanism involving H-atom

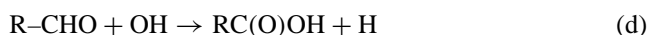
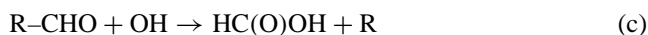
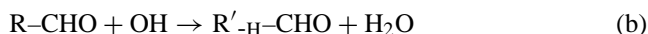
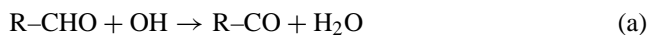
abstraction to explain their observation of PAN-formation from the room temperature reaction of OH with CH₃CHO in air in the presence of NO_x:



The major tropospheric transformation processes for the aliphatic aldehydes are photolysis and reaction with OH radicals, which themselves are mainly formed via the photodissociation of O₃ ($\lambda \leq 320$ nm). Reactions with O₃ have not been observed at room temperature, and the NO₃ radical and HO₂ radical reactions are of only minor importance in the troposphere [6]. The kinetics of the reaction of acetaldehyde with hydroxyl radicals have been investigated very often, but there are fewer data available on the reaction of propionaldehyde + OH. The recommended rate coefficients at room temperature are $1.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the acetaldehyde + OH reaction and $2.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for propionaldehyde + OH, only considering H-abstraction [7]. The existence of a negative temperature dependence for the

* Corresponding author. Tel.: +32-16-327382; fax: +32-16-327992.
E-mail address: jozef.peeters@chem.kuleuven.ac.be (J. Peeters).

k (aldehyde + OH) rate coefficients [7,8] could however imply a parallel addition/elimination reaction channel.



Several product studies have been carried out throughout the years to elucidate the reaction mechanism, with contradicting conclusions [9–14]. In the early 1990s, it was generally accepted that the reactions of aldehydes with hydroxyl radicals proceed dominantly by H-abstraction of the aldehydic H-atom for C₃–C₆ straight chain aldehydes and with the CH₂-group in β -position to the –CHO group being significantly activated [15], but it was still unclear from the observed negative temperature dependence of the rate coefficient if the reactions proceed through a direct H-atom abstraction or through addition/elimination with formation of a “long-lived” intermediate [2,16]. However, in 1996 Taylor et al. [17] proposed, based on both experimental work and quantum mechanical calculations, that at ambient and moderately elevated temperatures (295–600 K) the acetaldehyde+OH reaction proceeds mainly by OH-addition to the carbonyl-C, followed promptly by CH₃-elimination, whereas abstraction of the aldehydic H-atom would be a minor path, accounting for only some 10% of the observed rate at 295 K. Measured rate coefficients below 600 K exhibit a negative temperature dependence (as observed earlier [9,12,13]), whereas k -data above 600 K show a positive temperature dependence. Measurements at varying pressures confirm the lack of pressure dependence, as reported earlier by Michael et al. [13]. But, as pointed out by Stief et al. [18], pressure dependence in the formic acid route might not be observed if the addition complex proceeds to formic acid faster than it decomposes back to reactants. Thus, the addition reaction is not needed to explain any observations, but neither can it be ruled out.

An alternative explanation for the negative T-dependence of the rate coefficient near room temperature and for the absence of a pronounced D/H kinetic isotope effect [17] was suggested by Peeters [19] who proposed initial formation of a weak complex involving a hydrogen bond between the hydroxyl-H and the carbonyl-O. Provided the barrier for internal H-abstraction in this complex (shift of aldehyde-H to hydroxyl-O) is lower than the well depth of the complex, increase of the temperature will result in an increased fraction of redissociation of the H-bonded complex, and hence less product formation. A general scheme along these lines had earlier been proposed by Singleton and Cvetanović [20].

For the reaction of propionaldehyde with hydroxyl radicals, there are no data concerning the product distribution. It is assumed that the reaction proceeds via abstraction of the formyl H-atom [8,16]. Recently, Bercés et al. [21] carried out quantum mechanical calculations for this reaction

to characterize the potential energy surface. According to their work, the OH addition to the carbonyl-C and subsequent C₂H₅-elimination is unlikely to occur because of an entrance barrier for this path of about 16.5 kJ mol^{–1}.

Aiming to elucidate the reaction mechanism, experiments were set out to determine the quantitative importance of the H-abstraction paths (a + b) by direct measurement of the amount of H₂O that arises in the reactions of acetaldehyde and propionaldehyde with OH. Remark that abstraction of the more weakly bonded aldehyde H-atom from the formyl group is much more likely than the abstraction of the acetyl-type methyl hydrogens (bond strengths 365.3 and 385.5–397 kJ mol^{–1}, respectively [4,22]).

2. Experimental study

2.1. Experimental set-up and conditions

The H-abstraction contributions for the reactions of acetaldehyde and propionaldehyde were measured by means of a conventional multi-stage fast-flow reactor coupled to a molecular beam sampling mass spectrometry (MBMS) apparatus, as described earlier [23,24]. The reactor consists of a cylindrical quartz tube (internal radius $R = 1.35$ cm) equipped with a microwave-discharge side-arm and a set of two co-axial independently movable central injector tubes. Hydroxyl radicals were generated in the 5 cm long “preparation stage” of the reactor by reacting H atoms, created by dissociating H₂ in an upstream microwave discharge, with NO₂, added through the outer co-axial injector tube, according to the reaction $\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}$. The absolute H-atom concentration was determined from the decrease of the measured H₂⁺ signal when switching on the discharge, with absolute concentrations of H₂ derived from the measured flow of a certified high-purity gas mixture and the total pressure. In most experiments the initial concentration was $[\text{H}] \approx 2 \times 10^{13}$ molecule cm^{–3}. The added initial $[\text{NO}_2]_i$, as determined from its flow, was usually around 1×10^{13} molecule cm^{–3}, such that there was a moderate excess of H atoms, and the resulting initial OH-concentration could be taken equal to $[\text{NO}_2]_i$. The (remaining) H-atom concentration ($\sim 1 \times 10^{13}$ molecules cm^{–3}) ensures fast relaxation of any vibrationally excited OH ($v = 1, 2$) formed in the $\text{H} + \text{NO}_2$ reaction [25].

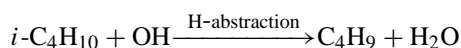
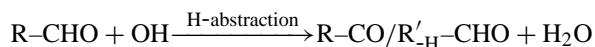
The reactor was treated, after cleaning, with a 10% HF solution to suppress radical loss on the walls. The investigated VOC compound is added to the OH-flow via the inner co-axial injector tube. All experiments were carried out at 290 K and a total reactor pressure of 2 Torr using He as carrier gas. The flow speed in the OH + organic compound reaction region was about 1650–1750 cm s^{–1}, and the length of that region was varied between 10 and 16 cm, resulting in an effective interaction time t_{eff} of ≈ 3 –7 ms, allowing for a mixing time of 2–3 ms.

The gas at the reactor exit is sampled through a 0.3 mm pinhole giving access to three differentially pumped low-pressure chambers. After mechanical modulation to allow phase-sensitive detection, the molecular beam enters the last chamber, which houses an electron-impact ionizer and a high-sensitivity extranuclear quadrupole mass spectrometer. A lock-in amplifier distinguishes the beam signal from the background ions.

Gases and mixtures, used without further purification, were He (99.9996%) as discharge-inlet carrier gas, He (99.995%) as additional carrier gas (both Indugaz), H₂ (5.0% in UHP He), isobutane (99.95%) (both L'Air Liquide) and NO₂ (2.50% in UHP He) (air products). Acetaldehyde and propionaldehyde (>99%) were purchased from FLUKA.

2.2. Methodology

The determination of the H-abstraction fraction has been done on a relative basis. A small amount of OH is reacted with a very large excess of the investigated aldehyde to ensure a fast and quantitative conversion of the OH into primary reaction products. The H₂O-signal measured for this reaction is compared with the H₂O-signal for the reaction of OH with a reference compound, measured under identical conditions, i.e. with the same input of OH radicals under the same experimental conditions. An ideal reference compound is one that gives 100% H-abstraction in the reaction with OH. It is well established that the reactions of alkanes with hydroxyl radicals near room temperature proceed solely via H-abstraction to produce H₂O and an alkyl radical [2]. Isobutane, which has a fairly high rate coefficient of $2.19 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [26] was chosen as reference compound in this work.



The H-abstraction fraction $f_{\text{H-abstraction}}$ of the aldehyde + OH reaction, relative to the reference reaction, is obtained from:

$$f_{\text{H-abstr}} = \frac{[\text{H}_2\text{O}]_{\text{aldehyde}}}{[\text{H}_2\text{O}]_{\text{isobutane}}}$$

For a given temperature, total pressure and average molecular mass of the gas in the reactor, the mass spectrometric output signal i_X is directly proportional to the absolute concentration $[X]_s$ of the given species at the sampling point: $i_X = S_X [X]_s$. The equation can therefore be re-written as:

$$f_{\text{H-abstr}} = \frac{i_{\text{H}_2\text{O, aldehyde}}}{i_{\text{H}_2\text{O, isobutane}}}$$

The measured H₂O⁺-signals ($i_{\text{H}_2\text{O, tot}}$) were corrected for H₂O-blank signals, resulting from H₂O formed in the titration zone predominantly by the wall reaction $\text{OH} + \text{H} \rightarrow$

H₂O (in conditions of excess [H] [27]), and from water vapor as impurity in the gases used:

$$i_{\text{H}_2\text{O, blank}} = i_{\text{H}_2\text{O, wall}} + i_{\text{H}_2\text{O, impurity}}$$

$$i_{\text{H}_2\text{O, formed}} = i_{\text{H}_2\text{O, tot}} - i_{\text{H}_2\text{O, blank}}$$

The measurement of the H₂O-signals was only started when the adsorption/desorption equilibrium of H₂O on the reactor walls was established, as evidenced by the H₂O⁺ signal having attained its asymptote. The H₂O⁺ signals were monitored at an ionizing energy of only 13.1 eV, i.e. slightly above the H₂O ionization potential of 12.65 eV, in order to suppress H₂O⁺ fragment ion formation from possible OH-adducts.

Because the sensitivity to H₂O is dependent to some extent on the average molecular mass of the gas in the reactor, non-reactive CO₂ was introduced into the system to keep the average molecular mass, and thus the H₂O-sensitivity, the same in the different reactions. This makes it possible to accurately compare the H₂O-signals of both reactions in the relative method.

The uncertainties on individual determinations are quite high, due to the fact that the total H₂O signals ($i_{\text{H}_2\text{O, tot}}$) have to be corrected for the blank signals ($i_{\text{H}_2\text{O, blank}}$), which were usually about half of the total H₂O signals, and due to the poor signal-to-noise ratio at the very low electron energy at which the H₂O signals had to be measured as explained above. Therefore, in order to obtain a statistically sufficient precision on the average result, the measurements were repeated a large number (≈ 10) of times, under (slightly) different conditions of input $[\text{OH}]_i$.

3. Results

The concentration ranges used in the experiments were $[\text{OH}]_i = (8.3\text{--}11.0) \times 10^{12} \text{ radicals cm}^{-3}$, remaining $[\text{H}]_i \approx 1 \times 10^{13} \text{ atoms cm}^{-3}$, $[\text{aldehyde}] = (0.6\text{--}1.9) \times 10^{15} \text{ molecules cm}^{-3}$ and $[\text{isobutane}] = (2.7\text{--}3.3) \times 10^{15} \text{ molecules cm}^{-3}$.

It can be calculated that in these conditions (i) the OH-consumption is already 99% complete in a time less than 1 ms, while $\approx 3\text{--}7$ ms is available; and (ii) the OH is removed solely by the primary reaction, while secondary reactions of OH are negligible. It was indeed found that the OH-signal at $t_{\text{eff}} = 3$ ms drops to zero upon addition of the aldehyde or isobutane.

Several determinations of the H₂O yield of the aldehyde + OH reactions were carried out. The individual measurements are given in Tables 1 and 2 for the acetaldehyde + OH and propionaldehyde + OH reaction, respectively. The listed H₂O_{formed} signals are already corrected for $i_{\text{H}_2\text{O, blank}}$ (including $i_{\text{H}_2\text{O, wall}}$).

For the reaction of acetaldehyde + OH, the weighted average result and the 1σ standard deviation for $f_{\text{H-abstraction}}$ over 12 measurements is $89 \pm 6\%$. For propionaldehyde + OH,

Table 1
Determination of the H-abstraction fraction for the acetaldehyde + OH reaction, using the relative method

[OH] _{initial} (10 ¹² cm ⁻³) ^a	H ₂ O-signals (μV) ^a		<i>f</i> _{H-abstraction} (%) ^a
	<i>i</i> _{H₂O, acetaldehyde} ^b	<i>i</i> _{H₂O, isobutane} ^b	
8.98 ± 0.45	14.05 ± 2.56	18.03 ± 2.79	78 ± 19
9.13 ± 0.46	22.62 ± 2.32	18.95 ± 2.12	119 ± 18
9.23 ± 0.46	20.72 ± 2.33	21.75 ± 3.19	95 ± 18
9.64 ± 0.48	18.95 ± 2.58	23.53 ± 2.73	81 ± 14
9.15 ± 0.46	16.40 ± 1.78	18.99 ± 2.31	86 ± 14
8.35 ± 0.42	12.09 ± 1.93	10.13 ± 1.83	119 ± 29
9.25 ± 0.46	10.02 ± 2.30	8.07 ± 2.10	124 ± 43
9.45 ± 0.47	13.19 ± 2.86	18.76 ± 3.22	70 ± 19
9.24 ± 0.46	13.22 ± 3.61	13.59 ± 3.23	97 ± 35
9.60 ± 0.48	15.22 ± 2.85	10.50 ± 3.06	145 ± 50
9.55 ± 0.48	12.85 ± 2.27	12.06 ± 2.42	107 ± 29
9.76 ± 0.50	11.26 ± 2.98	18.34 ± 0.185	61 ± 19

^a The reported uncertainties are 1σ standard deviations.

^b Corrected for *i*_{H₂O, blank} (including *i*_{H₂O, wall}).

seven experiments were performed with a weighted average result for *f*_{H-abstraction} of 100 ± 10%.

It was also attempted to quantify any HC(O)OH that would result in the addition/elimination process as proposed by Taylor et al. [17]. This was done by direct measurement of the HC(O)OH⁺-signal at mass 46 at electron energies of 15, 30 and 60 eV. The discharge on/off method was used to take into account isotopes of the aldehyde itself. No formic acid could be experimentally observed, thus if any formic acid is formed in this reaction, it is below the detection limit of our system. The detection limit for HC(O)OH was mainly determined by the contribution of (fragments of) isotopes of the aldehydes. No significant difference in the signals with and without discharge could be determined, and therefore it can be concluded that the yield of HC(O)OH is less than 3%. According to the theoretical studies of Taylor et al. [17] and Bercés et al. [21], the decomposition of the adduct RCH(OH)O to RC(O)OH + H will be even less important than the decomposition to R + HC(O)OH, due to the higher barrier.

Stabilization of the OH-adduct is highly unlikely given the very short lifetime (order of ps) of the chemically

Table 2
Determination of the H-abstraction fraction for the propionaldehyde + OH reaction, using the relative method

[OH] _{initial} (10 ¹² cm ⁻³) ^a	H ₂ O-signals (μV) ^a		<i>f</i> _{H-abstraction} (%) ^a
	<i>i</i> _{H₂O, propionaldehyde} ^b	<i>i</i> _{H₂O, isobutane} ^a	
9.55 ± 0.48	18.55 ± 4.33	28.64 ± 5.28	65 ± 19
9.49 ± 0.47	17.91 ± 3.12	15.26 ± 3.72	117 ± 35
9.90 ± 0.50	21.23 ± 2.86	20.02 ± 2.99	106 ± 21
10.3 ± 0.50	24.97 ± 2.41	16.96 ± 2.70	147 ± 27
10.5 ± 0.50	14.51 ± 2.89	14.05 ± 3.33	103 ± 32
9.70 ± 0.49	12.15 ± 3.03	13.36 ± 3.36	91 ± 32
9.25 ± 0.46	13.83 ± 2.97	13.83 ± 2.79	108 ± 33

^a The reported uncertainties are 1σ standard deviations.

^b Corrected for *i*_{H₂O, blank} (including *i*_{H₂O, wall}).

activated hydroxy adduct for dissociation to R + HC(O)OH [24]. Given the low decomposition barrier of the α-hydroxyalkoxy radicals of only 29–33.5 kJ mol⁻¹ [21,24], even the thermal decomposition should occur at a rate >10⁶ s⁻¹. This also precludes any pressure effect on a possible addition/elimination pathway. Experimentally, no evidence for stabilized adducts was found.

4. Discussion

It is concluded from these results that at ambient temperatures the reaction of aldehydes with OH radicals proceeds quasi-exclusively by H-abstraction to form H₂O.

Very recent work confirms these findings. Tyndall et al. [28] used a photoreactor combined with FTIR to investigate the formation of acids in the reaction of OH radicals with acetaldehyde in 1 atmosphere of air at 296 and 251 K. They found no evidence for direct formation of either formic or acetic acid (<10% yield) and therefore they concluded that under atmospheric conditions the reaction of OH radicals with acetaldehyde proceeds predominantly (>90%), if not exclusively, via H-atom abstraction. Cameron et al. [29] studied the reaction of acetaldehyde + OH by monitoring the possible product radicals CH₃CO, CH₃ and H. CH₃CO was detected at high yield (0.94 ± 0.19); CH₃ radicals were not formed in the time-scale of the reaction (<0.03 at 298 K) and H-atoms were not observed for this reaction (<0.02 at 298 K). Recently, Alvarez-Idaboy et al. [30] characterized the reaction of acetaldehyde + OH using ab initio methods with large basis sets. A negative activation energy value is obtained for the acetaldehyde + OH reaction. The results clearly indicate that the reaction occurs by hydrogen abstraction, that the OH-addition channel is unfavorable and that the most likely reaction pathway for OH with aldehydes involves a loose H-bonded complex which does not lead to addition to the carbonyl double bond. These calculations of Alvarez-Idaboy et al. [30] and also those of Aloisio and Francisco [31] confirm a suggestion which was already made as early as 1976 by Singleton and Cvetanović [20], who described successfully the behavior of reactions having a negative temperature dependence by proposing a complex mechanism and explained the occurrence of negative activation energies as being due to the reversible formation of a loosely bound pre-reactive complex which is formed without activation energy, followed by a second reaction, which is irreversible, and whose transition state is lower than the energy of the separate reactants.

It can be concluded that the addition of OH to the >C=O double bond is excluded because its activation energy is much higher than the one for hydrogen abstraction. The aldehyde H-atom has a relatively low bond energy, while the addition of OH to the carbon atom is unfavorable. The addition of OH to the carbonyl carbon atom was shown to be an exothermic reaction with ab initio estimated barrier

heights of 20–40 kJ mol⁻¹ [21,30,32,33]. For the analogous reaction of acetone+OH, a B3LYP-DFT/6–31G(d, p) barrier for the OH-addition to the carbonyl double bond of 25 ± 2 kJ mol⁻¹ was calculated by our group and transition state theory calculations on the rate of the OH-addition lead to a rate coefficient at room temperature of only $k(298\text{ K}) = 1 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [24].

The proposed indirect H-abstraction mechanism provides a clear explanation of the experimental behavior. If the barrier of the reverse of the first step is larger than the barrier for the second step, the former will be relatively more favored by an increase in temperature, and the overall rate will decrease. In the aldehydes + OH reactions the effective negative activation energy is well established [7].

It can be readily argued that the contribution of abstraction of the acetyl-hydrogens from CH₃CHO should be negligible compared to the aldehyde-H-abstraction. The total rate coefficient is nearly 100 times larger than that for the OH reaction with CH₃COCH₃ [7], which has two methyl groups that are similar in every respect to the methyl in CH₃CHO; the C–H bond strengths are quasi-identical [34] and the abstraction of a methyl-H leads to vinyloxy-type resonance stabilization for both molecules. Thus, clearly, it is the weakly bonded aldehyde-H that sets CH₃CHO apart from CH₃COCH₃, and that lends CH₃CHO its much higher reactivity. This reasoning was recently confirmed experimentally by Cameron et al. [29].

5. Conclusion

Commonly used photochemical models, assuming CH₃CO to be the sole primary-product of the acetaldehyde+OH reaction, apparently overpredict atmospheric PAN compared to measurements [35] and this was considered to be indirect support for the view of a parallel addition/fragmentation channel yielding a carboxylic acid and an alkyl radical as concluded by Taylor et al. [17]. However, the experimental results obtained in this work show that reactions of aldehydes (RCHO) with OH at 290 K yield quasi-exclusively H₂O+RCO. It is argued that H-abstraction from the methyl group of CH₃CHO can account for only ≈1% of the total H-abstraction rate. For both CH₃CHO and C₂H₅CHO + OH, we could not detect any production of HC(O)OH, which according to the addition/fragmentation scheme proposed by Taylor et al. [17] should be the major reaction product. Allowing for signal noise, etc., we put an upper limit of ≈3% to the contribution of this channel. Thus, the overall process results in H-abstraction, although the temperature dependence indicates that the reaction proceeds through an initial, pre-reactive complex. It was suggested, and confirmed by recent theoretical studies, that the reactions of aldehydes + OH proceed by a loosely bonded H-complex, which facilitates the reaction, leading to negative temperature dependences.

Acknowledgements

The authors thank the Belgian Federal Office for Science, Technology and Culture for support of this research in the frame of the Belgian programme on Global Change and Sustainable Development. SV is indebted to the Flemish Institute for Science and Technology (IWT) for granting her a doctoral fellowship. At present SV has a postdoctoral grant on the UTOPIHAN-ACT EC project in the Fifth Framework Programme. JP thanks the Fund for Scientific Research Flanders (FWO-Vlaanderen) and the KULeuven Research Council (BOF Fund) for continuing support.

References

- [1] A. Guenther, C.N. Hewitt, D. Erickson, R. Fall, C. Geron, T. Graedel, P. Harley, L. Klinger, M. Lerdau, W.A. McKay, T. Pierce, B. Scholes, R. Steinbrecher, R. Tallamruja, J. Taylor, P. Zimmerman, J. Geophys. Res. (Atm) 100 (1995) 8873.
- [2] R. Atkinson, J. Phys. Chem. Ref. Data, Monograph 2 (1994) 1.
- [3] A.C. Lloyd, NBS Special Pub. 557 (1979) 27, and references therein.
- [4] B.J. Finlayson-Pitts, J.N. Pitts Jr., Chemistry of the Upper and Lower Atmosphere—Theory, Experiments and Applications, Academic press, San Diego, 2000.
- [5] R. Atkinson, A.C. Lloyd, J. Phys. Chem. Ref. Data 13 (1984) 315.
- [6] R. Atkinson, Issues in environmental science and technology: 4. Volatile organic compounds in the atmosphere, in: E.R. Hester, R.M. Harrison (Eds.), Royal Society of Chemistry, Cambridge, 1995.
- [7] R. Atkinson, D.L. Baulch, R.A. Cox, R.F. Hampson, J.A. Kerr, M.J. Rossi, J. Troe, J. Phys. Chem. Ref. Data 28 (1999) 191.
- [8] R. Thévenet, A. Mellouki, G. Lebras, Int. J. Chem. Kinet. 32 (2000) 676.
- [9] R. Atkinson, J.N. Pitts Jr., J. Chem. Phys. 68 (1978) 3581.
- [10] E.D. Morris, H. Niki, J. Phys. Chem. 75 (1971) 3640.
- [11] E.D. Morris Jr., D.H. Stedman, H. Niki, J. Am. Chem. Soc. 93 (1971) 3570.
- [12] D.H. Semmes, A.R. Ravishankara, C.A. Gump-Perkins, P.H. Wine, Int. J. Chem. Kinet. 17 (1985) 303.
- [13] J.V. Michael, D.G. Keil, R.B. Klemm, J. Chem. Phys. 83 (1985) 1630.
- [14] H. Niki, P.D. Maker, C.M. Savage, L.P. Breitenbach, J. Phys. Chem. 88 (1984) 5342.
- [15] E.S.C. Kwok, R. Atkinson, Atmos. Environ. 29 (1995) 1685.
- [16] C. Papagni, J. Arey, R. Atkinson, Int. J. Chem. Kinet. 32 (2000) 79.
- [17] P.H. Taylor, M.S. Rahman, M. Arif, B. Dellinger, P. Marshall, in: Proceedings of Twenty-Sixth Symposium (International) on Combustion, vol. 26, 1996, p. 497.
- [18] L.J. Stief, D.F. Nava, W.A. Payne, J.V. Michael, J. Phys. Chem. 73 (1980) 2254.
- [19] J. Peeters, in: U. Schurath, R. Roselieb (Eds.), Proceedings of the Second Workshop of the Eurotrac-2 Subproject Chemical Mechanism Development (CMD), FZK-Proceedings 98-01, 1998, p. GPP1.
- [20] D.L. Singleton, R.J. Cvetanović, J. Am. Chem. Soc. 98 (1976) 6812.
- [21] T. Bercés, et al., private communication.
- [22] D.F. McMillen, D.M. Golden, Ann. Rev. Phys. Chem. 33 (1982) 493.
- [23] J. Peeters, S. Vandenberk, E. Piessens, V. Pultau, Chemosphere 38 (1999) 1189.
- [24] S. Vandenberk, L. Vereecken, J. Peeters, Phys. Chem. Chem. Phys. 4 (2002) 461.
- [25] J.E. Spencer, G.P. Glass, Chem. Phys. 15 (1976) 35.
- [26] R. Atkinson, D.L. Baulch, R.A. Cox, R.F. Hampson Jr., J.A. Kerr, M.J. Rossi, J. Troe, J. Phys. Chem. Ref. Data 26 (1997) 1329.
- [27] R. Zellner, K. Erler, D. Field, in: Proceedings of Sixteenth Symposium (International) on Combustion, vol. 16, 1976, p. 939.

- [28] G.S. Tyndall, J.J. Orlando, T.J. Wallington, M.D. Hurley, M. Goto, M. Kawasaki, *Phys. Chem. Chem. Phys.* 4 (2002) 2189.
- [29] M. Cameron, V. Sivakumaran, T.J. Dillon, J.N. Crowley, *Phys. Chem. Chem. Phys.* 4 (2002) 3628.
- [30] J.R. Alvarez-Idaboy, N. Mora-Diez, R.J. Boyd, A. Vivier-Bunge, *J. Am. Chem. Soc.* 123 (2001) 2018.
- [31] S. Aloisio, J.S. Francisco, *J. Phys. Chem. A* 104 (2000) 3211.
- [32] M.R. Soto, M. Page, *J. Phys. Chem.* 94 (1990) 3242.
- [33] I.M. Borisov, D.A. Mikhailov, S.L. Khursan, V.M. Yanborisov, *Russ. J. Chem. Phys.* 72 (1998) 1603.
- [34] L. Vereecken, J. Peeters, *Phys. Chem. Chem. Phys.* 4 (2002) 467.
- [35] J.M. Roberts, R.L. Tanner, L. Newman, V.C. Bowersox, J.W. Bottenheim, K.G. Anlauf, K.A. Brice, D.D. Parrish, F.C. Fehsenfeld, M.P. Bühr, J.F. Meagher, E.M. Bailey, *J. Geophys. Res. (Atm)* 100 (1995) 22821.