

Kinetics and dynamics of unimolecular reactions of alkoxy radicals at elevated temperatures: A combined quantum chemical / RRKM dynamical study.

Holger Somnitz*, Reinhard Zellner
Institute of Physical and Theoretical Chemistry
University of Duisburg-Essen
45117 Essen, Germany

Abstract

The present work provides quantitative results for the rate coefficients of unimolecular alkoxy radical reactions at elevated temperatures up to 1500 K and in the pressure range 0.1 mbar to 10^4 bar. Of particular relevance are changes of the relative importance of different reaction channels. This is evident for longer chain alkoxy radicals which at lower temperatures undergo isomerisation via an energetically favourable six-member ring transition state. At temperatures above >600 K, however, the rates of the decomposition pathways can become faster than that of isomerisation.

The approach which we have used in our studies makes use of extensive (G2/G3) ab initio calculations. These are utilised as input for a subsequent multichannel RRKM/ME (master equation) treatment which yields rate coefficients and complete fall-off curves for arbitrary pressure and temperature conditions. The kinetics of two exemplarily chosen straight chain linear alkoxy radicals, 1-butoxyl and 2-pentoxyl, have been analysed to show the complex temperature and pressure behaviour resulting from the competition of multiple accessible reaction channels each with its own and different p,T -dependence. Additional results are reported for the minimum temperatures where channel switching can occur, the trajectory of these characteristic points on the p,T – surface, and the temperature dependence of the fractional ratios of the unimolecular reaction channels among each other and the bimolecular reaction with oxygen (at ambient pressure).

Introduction

Oxygenated radicals such as peroxy radicals, oxy radicals and hydroxy substituted alkyl radicals are thought to play an important role in the combustion of hydrocarbons in the intermediate and low combustion temperature regime. Of these radicals alkoxy radicals are of particular interest since they exhibit branching reactions leading either to stable carbonyl or isomerisation products [1-3].

The needs to model flame properties require accurate kinetic data over extended ranges of pressure and temperature for a rich manifold of chemical species. Since it is foreseeable that not all of these can be obtained experimentally, theoretical approaches have become useful and accepted alternatives both with respect to accuracy and predictive power.

In a first step, the current work shows an extension of former results from our group, which were initially obtained for conditions prevailing in the troposphere. Absolute rate coefficients for the unimolecular reaction channels of two exemplarily chosen linear alkoxy radicals, 1-butoxyl and 2-pentoxyl, are presented as well as their relative importance among each other and compared to the bimolecular reaction with O_2 .

Depending on the structure of the alkoxy radical they show up to four distinct competitive reaction pathways [5]: (i) reaction with O_2 , yielding an aldehyde or a ketone and HO_2 , (ii/iii) unimolecular decomposition, forming an aldehyde and an alkyl radical, and (iv) isomerisation via a 6-membered

transition state (1,5-H-shift). All four reactions are possible for the 2-pentoxyl radical which may be considered a prototype for this class of reactions. In addition we show results for the 1-butoxyl, which allows only one relevant decomposition pathway but also has the ability to isomerise via (1,5-H-shift). Under ambient atmospheric conditions these isomerisation reactions, if possible, are known to proceed by at least one to two orders of magnitude faster than the decomposition channels. The possible reactions are shown schematically in Fig. 1 using the 2-pentoxyl radical as example.

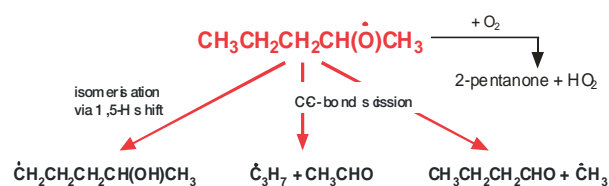


Fig. 1. Relevant reaction pathways for the 2-pentoxyl radical.

Since the temperature dependence of the bimolecular channel with O_2 is small, this reaction loses importance rapidly as the rates of the unimolecular reaction channels increase with increasing temperature.

Theoretical methods

In order to predict the complete temperature and pressure dependence of the different unimolecular

* Corresponding author: holger.somnitz@uni-essen.de
Associated Web site: <http://www.uni-essen.de/iptc/>
Proceedings of the European Combustion Meeting 2005

reaction channels large scale *ab initio* calculations have been performed. The resulting molecular data were used in a combined RRKM/master-equation (ME) treatment to determine fall-off curves at arbitrary temperatures. All Arrhenius fits and expressions are derived from the “numerically exact” rate coefficients and are valid in the specified temperature and pressure ranges only.

Quantum chemical calculations

Since this paper is primarily intended to present new kinetic data, only a brief outline of the quantum chemical calculations performed will be given. Further details can be found in the original publications [4,5]. As one result of these extensive studies we prefer the use of MP2(Full)/6-31G(d) optimised geometries for species containing only C, H, and O constituents and at least double bonds to rely subsequent single point calculations of the G2/G3-type thereon. Although we were able to increase the computational level from the G2(MP2,SVP) level of theory to somewhat more modern G3 or, alternatively small to mid scale CCSD(T) calculations using up to cc-pVTZ basis sets, we find no significant increase in the estimated accuracy of our barriers E_0 for reaction which are the most important single parameter for the subsequent kinetic calculations. Interestingly, the general thoughts which inspired us several years ago to use a slightly modified G2(MP2,SVP) instead of the original G2(MP2) method could be found in the evolution of the current G3-theory. In particular, the replacement of the QCISD(T)/6-311G(d,p) calculation by one using the smaller 6-31G(d) basis set is thought to give even more balanced results in conjunction with the additive terms which make up the complete G2/G3 energy. Our former results as performed in the original paper [4] could be considered as nearly identical or slightly superior to the current G3(MP2) level. Therefore we stay with the original data and keep the comparability with the rate coefficients obtained from them for tropospheric conditions in the temperature range $220\text{K} < T < 300\text{K}$ [5].

This work has also been part of a comprehensive study of, up to this point, linear alkoxy radicals in general. In the course of this a microscopic SAR could be developed that clarifies in a general manner the most important aspects of the reactivity of alkoxy radicals [6].

Statistical kinetic calculations

The most important data used in the statistical calculations comprise the quantum chemically derived (scaled MP2) frequencies, the critical energy barriers (E_0), the rotational constants (B , B^\ddagger) of all relevant molecular configurations, and the information on interaction with the bathgas N_2 assuming a Lennard-Jones potential. A complete set of data as well as more details of the geometries can be found elsewhere [4,5].

From these data densities and sums of states were calculated and energy specific rate coefficients $k(E)$ for every unimolecular reaction channel were determined

by use of a statistical approach. We applied the standard RRKM expression, *viz.* [7]

$$k(E) = [h\rho(E)]^{-1} \sum_0^{E-E_0} P^\ddagger(E_+)$$

whereas the J -dependence have been dropped because all reactions considered proceed across significant barriers and tight transition states along the intrinsic reaction path. Therefore, the best position of the dividing surface (the so-called point of no return in transition state theory), which is used to evaluate the nominator in the RRKM-formula, is sufficiently determined by the quantum chemically calculated saddlepoint on the potential energy surface.

Furthermore, the release of additional rotational energy in the reaction coordinate due to the conservation of angular momentum is small since the rotational constants of the equilibrium and transition state configurations are of similar value. Nevertheless, the effect of conservation of angular momentum is taken into account correctly in the high pressure limit by the factor $B_{xx,yy}/B_{xx,yy}^\ddagger$ of the rotational constants for the adiabatic external rotations.

In the next step the pointwise solution of a one-dimensional master equation, *viz.* [7]

$$\lambda n(E) = - \sum_i k_i(E) + \omega \int_0^\infty (P_{E' \rightarrow E} n(E') - P_{E \rightarrow E'} n(E)) dE'$$

relates the microscopic rate coefficients $k_i(E)$ to the thermal ones $k_i(p,T)$. In the simple case of a single channel reaction the largest eigenvalue is identified as the thermal rate coefficient via $\lambda = -k_{\text{uni}}$ corresponding to the eigenfunction $n(E)$ which denotes the population of the microcanonical ensemble with energy E . ω denotes the collision frequency and $P_{E \rightarrow E'}$ is the probability of collisional energy transfer from a state with internal energy E to one with internal energy E' . For $P_{E \rightarrow E'}$ a displaced Gaussian was used arising from Biased Random Walk theory [7] which was also used to estimate the moments of this distribution such as the energy transfer parameter $\langle E_{\text{down}} \rangle$. In each case we assume N_2 as third body collider. The details of the complete treatment are described elsewhere [5].

Using this approach we are able to calculate rate constants under arbitrary conditions in an *a priori* manner and with predictive capabilities. This has been proven in several instances by recent experiments mostly performed in temperature ranges between 280 and 350 K. See for example current work on the decomposition of 2-butoxyl [7,8] and the isomerisation of 2-pentoxyl [9] which compare nicely with our *a priori* predictions.

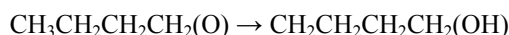
Results and Discussion

As outlined above, we take care of the simultaneous occurrence of multiple reaction channel by setting up a multi-channel master equation and coupling the possible unimolecular reaction pathways. Thus, solving for the

eigenfunction $n(E)$ rather than for the eigenvalue λ permits the determination of the absolute rate coefficients for each reaction channel individually. This procedure has to be performed for each combination of temperature and pressure of interest. We have obtained solutions for temperatures between 220 and 1500 K and in each case for sufficient discrete pressures to show fall-off curves of continuous shape.

1-Butoxyl radicals

We considered the 1-butoxyl radical in first place since it constitutes the smallest alkoxy radical exhibiting the possibility to isomerise via 1,5-H shift forming the delta-hydroxy-butyl radical, *viz.*



In addition, its treatment is somewhat less complex than that of the 2-pentoxyl radical. The corresponding barrier to isomerisation had been calculated to $E_0 = 42.7$ kJ/mol, whereas the decomposition channel, which leads to the formation of a propyl radical and formaldehyde via C-C bond rupture, is energetically in disfavour by roughly 20 kJ/mol showing a barrier of $E_0 = 62.8$ kJ/mol.

Figures 2a and 2b show the pressure and temperature dependence of the calculated rate coefficients. Complete fall-off curves are shown for temperatures between 300 and 1500 K in steps of 100 K.

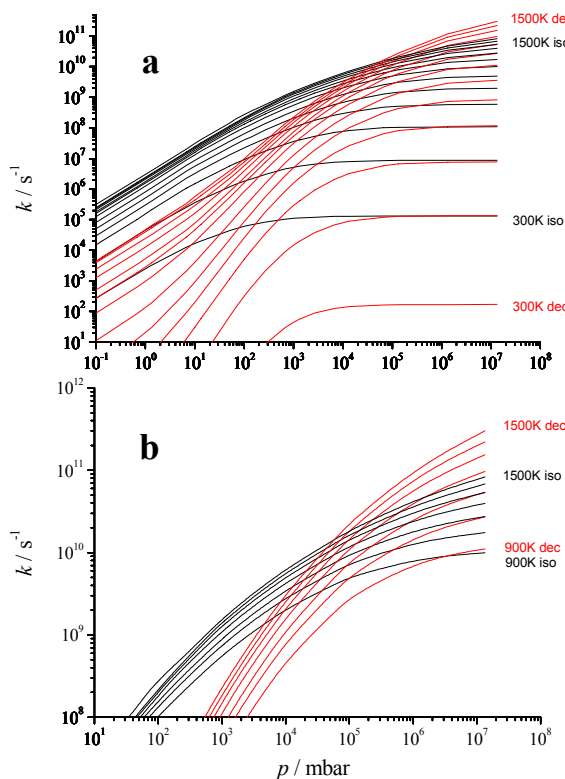


Fig. 2. (a) Fall-off curves of the isomerisation and decomposition of 1-butoxyl radicals for different temperatures between 300 and 1500 K in steps of $\Delta T=100$ K. (b) Fall-off curves enlarged.

A pressure range from 0.1 mbar up to 10^4 bar is shown to assure that the low and high pressure limiting regions are encompassed at least for the lower temperatures. Nevertheless, by the use of our input data, rate constants can be obtained easily at arbitrary temperatures and pressures and for a wide variety of bathgases. Fig. 2b takes a closer look to the region where the crossover in the rates of isomerisation vs. decomposition occurs. In case of the 1-butoxyl radical both channels are energetically very well separated. For the temperatures investigated we found the relevant pressures in the range of 10^2 to 10^3 bar.

It could be expected that, provided the isomerisation and decomposition pathways are energetically less separated as could be the case for larger alkoxy radicals and substituted alkoxy radicals, the same behaviour will occur at much lower pressures. The minimum temperature for the onset of the decomposition rate to dominate isomerisation could be derived by investigation of the high pressure limit. Here both reaction channels reach their undisturbed (thermal) maximum. Fig. 3 shows the temperature dependence of k^∞ for both reaction channels. The Arrhenius fits performed to our numerically data are very well represented by straight lines yielding Arrhenius activation energies of 42.2 and 67.2 kJ/mol, respectively. We find the minimum temperature where decomposition dominates isomerisation at a temperature of $T = 874$ K given by the intersection of the two linear Arrhenius-fits. Under all but high pressure conditions this intersection must be found at significantly higher temperatures.

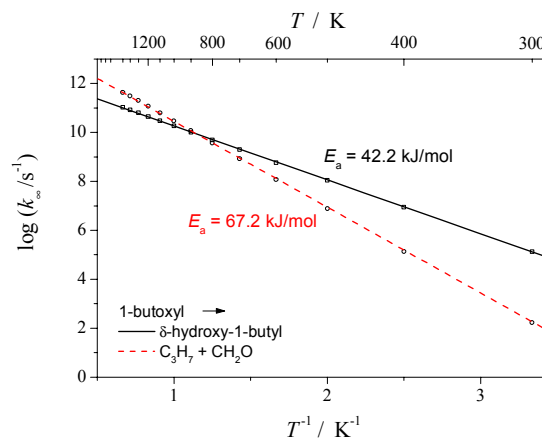


Fig. 3. Arrhenius plot of the high pressure limiting rate constants for decomposition and isomerisation of the 1-butoxyl radical.

Based on our calculated rate data we extract the following linear Arrhenius expression for the high pressure rate coefficients ($220 \text{ K} < T < 1500 \text{ K}$):

$$k_{\text{iso}}^\infty = 2.96 \times 10^{12} \exp(-5078 \text{ K}/T) \text{ s}^{-1}$$

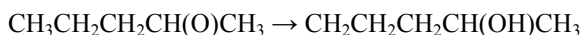
$$k_{\text{dec}}^\infty = 9.18 \times 10^{13} \exp(-8079 \text{ K}/T) \text{ s}^{-1}$$

Although not discussed in detail here, the predicted rates are in satisfactory agreement with the spread of

data gained from the available experiments performed on 1-butoxyl radicals [11-14] and otherwise theoretical work [15,16]. Recommendations and discussion of the corresponding rate coefficients can be found in [5] and somewhat more restricted to ambient conditions ($p \cong 1013$ mbar, $T \cong 298$ K) in recent reviews [3] and data collections [17,18].

2-Pentoxyl radicals

Whereas the 1-pentoxyl radical shows exactly the same possibilities for unimolecular isomerisation and decomposition as it is the case for the 1-butoxyl, we choose the 2-pentoxyl as the smallest prototype for the simultaneous occurrence of the maximum of three reaction pathways. Again, the energetically most favoured channel is the isomerisation via 1,5 H shift ($E_0 = 38.4$ kJ/mol) proceeding via a 6-membered cyclic transition state. In course of the isomerisation an H-atom is abstracted from a CH_3 -group which leads to a δ -hydroxy-1-pentyl radical, *viz.*



The decomposition channels yield either acetaldehyde and n-propyl ($E_0 = 50.7$ kJ/mol) or, more unfavoured, butanal and methyl ($E_0 = 62.4$ kJ/mol). To illustrate the complex nature of the temperature and pressure dependencies encountered Figures 4a and 4b provide an overview and a closer look on the crossover region, respectively.

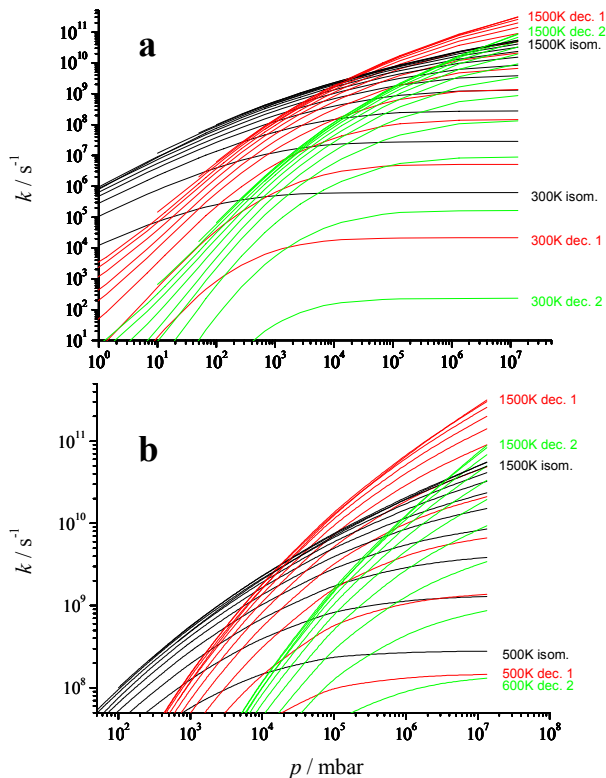


Fig. 4. (a) Fall-off curves of the isomerisation and the two different decomposition reactions of 2-pentoxyl radicals for different temperatures between 300 and 1500K in steps of $\Delta T=100$ K. (b) Fall-off curves enlarged.

In case of the 2-pentoxyl radical the interplay of the different reaction channels now yields two crossover points in our temperature region investigated. The first when decomposition into acetaldehyde and n-propyl overtakes isomerisation and the second - at higher temperatures and pressures - when the decomposition yielding butanal and methyl catches up with the isomerisation rates under this conditions too.

By examination of the high pressure limit of all three reaction channels we obtained the corresponding minimum temperatures where a crossover can occur. We find the relevant minimum temperatures to be 585 and 994 K. This is shown in the Arrhenius plot presented in Fig. 5, with the Arrhenius expressions given by:

$$\begin{aligned} k_{\text{iso}}^{\infty} &= 2.93 \times 10^{12} \exp(-4594 \text{ K}/T) \text{ s}^{-1} \\ k_{\text{dec}}^{\infty} &= 9.52 \times 10^{13} \exp(-6631 \text{ K}/T) \text{ s}^{-1} \\ k_{\text{dec}}^{\infty} &= 8.59 \times 10^{13} \exp(-7951 \text{ K}/T) \text{ s}^{-1} \end{aligned}$$

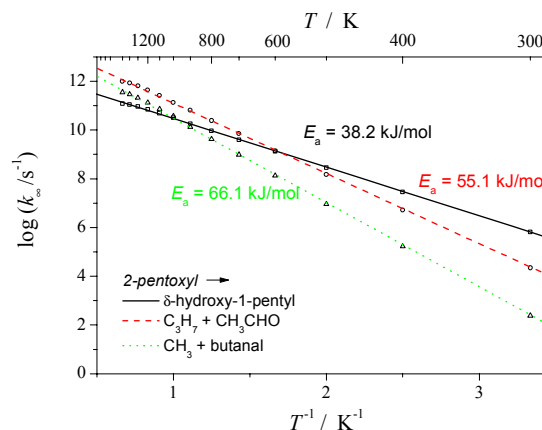


Fig. 5. Arrhenius plot of the high pressure limiting rate constants for isomerisation and the two decomposition reactions of the 2-pentoxyl radical.

It is obvious from Fig. 5 that at considerably higher temperatures than 1500 K another point could be reached when the so far unimportant decomposition into butanal and methyl reaches the rate of the energetically more favoured decomposition (into acetaldehyde and n-propyl). In the current study this effect has not been investigated further.

Literature data and absolute rate coefficients for the different 2-pentoxyl reaction channels are scarce. Under ambient atmospheric conditions Atkinson et al. [20] obtained a value of $2.5 \times 10^5 \text{ s}^{-1}$ for the isomerisation reaction in a relative rate experiment. This is by a factor of 2 slower than our result of $5.0 \times 10^5 \text{ s}^{-1}$. Another very recent experimental study was performed by Johnson et al. [10]. They investigated the temperature dependence of the 2-pentoxyl isomerisation and obtained a rate of $(5.2 \pm 1.8) \times 10^5 \text{ s}^{-1}$ at $T = 303$ K and ambient pressure which is nearly identical to our result calculated some years ago [5] and which is now extended to the higher temperatures.

For the decomposition channel yielding acetaldehyde and n-propyl we also find good agreement

with the rates obtained by Dóbé et al. [19] in another relative measurement. Their rate coefficient of $1.2 \times 10^4 \text{ s}^{-1}$ compares again nicely with our value of $1.0 \times 10^4 \text{ s}^{-1}$ calculated for ambient conditions.

Further Results

In the preceding two sections we have derived a near complete description of the unimolecular kinetics of the 1-butoxyl and 2-pentoxyl radicals. Based on this data other quantities of interest can be deduced. In Fig. 6 we summarise our findings on the temperatures and pressures where “channel-switching” occurs and show the path of the corresponding (p, T) values characterising this crossing point on the two-dimensional p, T - surface.

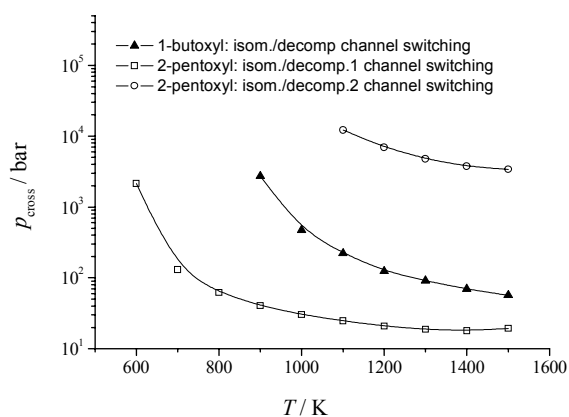


Fig. 6. Evolution of the (p, T) -conditions defining the different curve crossing points with increasing temperature for the unimolecular reactions of 1-butoxyl and 2-pentoxyl radicals.

Obviously, fairly high pressures are needed to see the decomposition rate coefficients dominating the isomerisation ones even at high temperature.

Of more applied interest are the relative fractions of the accessible reaction channels compared to the total reaction rate. Therefore, we fixed the total pressure to 1 bar and derived the temperature dependence of the fractional ratios of the unimolecular reaction channel among each other and the bimolecular reaction with oxygen (cf. Fig. 7). To calculate the rate coefficients for the bimolecular channels we have used the recommendations of Atkinson [21] for the reaction of O_2 with primary ($6.0 \times 10^{14} \exp(-550\text{K}/T) \text{ cm}^3 \text{ s}^{-1}$) and secondary alkoxy radicals ($1.5 \times 10^{14} \exp(-200\text{K}/T) \text{ cm}^3 \text{ s}^{-1}$). These were transformed to first order rate coefficients by assuming the partial pressure of oxygen in air at a total pressure of 1 bar.

We first note the channel switching between the bimolecular reaction with oxygen towards the dominance of the isomerisations when going from temperatures around 200 K to 300 K. Above this temperatures, although not quite as spectacular as a complete channel switching, the decomposition reactions gain in importance significantly as the temperature is raised further. For the temperature interval between 300 to 1500 K we note an increase of the fractional ratios of the decomposition channels

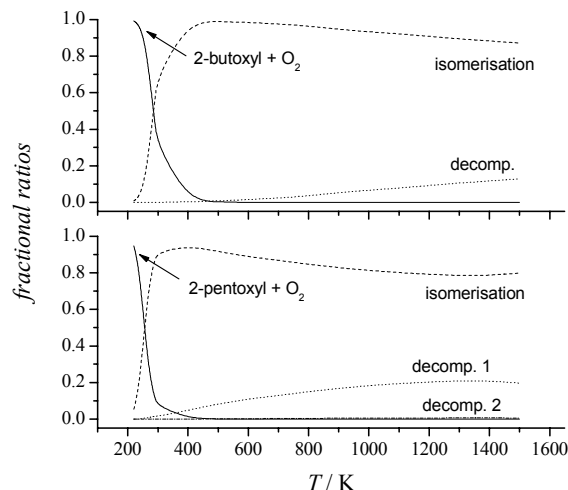


Fig. 7. Temperature dependence of the fractional ratios of the specified reactions to the corresponding sum of available reaction channels for the 1-butoxyl and the 2-pentoxyl radical, respectively. The total pressure assumed is $p = 1$ bar (bath gas N_2).

from 0 to 13% for 1-butoxyl and from 1-2% to 21% for 2-pentoxyl. These relative fractions will become larger with higher temperature and with higher pressures.

Conclusions

The rate coefficients for the unimolecular reactions of 2-pentoxyl and 1-butoxyl were investigated using a purely theoretical approach. The results obtained indicate the importance of a detailed description of all accessible pathways in a coupled manner and the sensibility of the branching ratios with variations in temperature and to a lower degree with pressure. The pressure effect is most noticeably if rate coefficients for the non-dominating pathways are required for pressures other than the high pressure limit. In general a much stronger decrease must occur compared to a standard treatment which only accounts for every reaction independent of the others. The reason is the competition with the dominating reaction channel which in general by reaction depopulates energy levels which otherwise could have contributed to the reaction with the higher energy barrier (the non-dominating channels). This very general pressure dependent behaviour of multichannel reactions could not be described by simple expressions such as the Troe formalism. Therefore, it is also not accounted for in the modelling of complex reaction mechanisms such as combustion systems. The problem gets even worse when the temperature dependence of the different reaction channels leads to a switching of the dominance among them. In these cases the pressure and temperature dependence leads to a complicated behaviour of the rate coefficients which can not be foreseen just by knowledge of the high and low pressure limiting rate constants and their idealized temperature behaviour. The elaborate calculations for our prototype molecules 1-butoxyl and 2-pentoxyl address these problems and illustrate the possibility but also the

complexity to find the correct rate coefficients and branching ratios for conditions where no direct experimental data are available.

References

- [1] R. Zellner, *Global Aspects of Atmospheric Chemistry*, Steinkopff, Darmstadt, 1999.
- [2] R. Atkinson, *J. Phys. Chem. Ref. Data*, 1994, Monograph 2, 1.
- [3] J.J. Orlando, G. S. Tyndall, T. J. Wallington, *Chem. Rev.* 103 (2003) 4657-4689.
- [4] H. Somnitz, R. Zellner, *Phys. Chem. Chem. Phys.* 2 (2000) 1899-1905.
- [5] H. Somnitz, R. Zellner, *Phys. Chem. Chem. Phys.* 2 (2000) 1907-1918.
- [6] H. Somnitz, R. Zellner, *Phys. Chem. Chem. Phys.* 2 (2000) 4319-4324.
- [7] R. G. Gilbert, S. C. Smith, *Theory of Unimolecular and Recombination Reactions*, Blackwell Scientific, Oxford, 1990.
- [8] H.G. Libuda, O. Shestakov, J. Theloke, F. Zabel, *Phys. Chem. Chem. Phys.* 4 (2002) 2579-2586.
- [9] G. Falgayrac, F. Caralp, N. Sokolowski-Gomez, P. Devolder, C. Fittschen, *Phys. Chem. Chem. Phys.* 6 (2004) 4127-4132.
- [10] D. Johnson, P. Cassanelli, R. A. Cox, *J. Phys. Chem. A* 108 (2004) 519-523.
- [11] W. P. L. Carter, A. C. Lloyd, J. L. Sprung, J. N. Pitts, *Int. J. Chem. Kinet.* 11 (1979) 45-101.
- [12] R. A. Cox, K. F. Patrick, S. A. Chant, *Environ. Sci. Technol.* 15 (1981) 587-592.
- [13] A. P. Altshuller, *J. Atmos. Chem.* 12 (1991) 19-61.
- [14] A. Heiss, K. Sahetchian, *Int. J. Chem. Kinet.* 28 (1996) 531-544.
- [15] T. P. W. Jungkamp, J. N. Smith, J. H. Seinfeld, *J. Phys. Chem. A* 101 (1997) 4392-4401.
- [16] G. Lendvay, B. Viskolcz, *J. Phys. Chem. A* 102 (1998) 10777-10786.
- [17] R. Atkinson, D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, Jr., J. A. Kerr, M. J. Rossi, J. Troe, *J. Phys. Chem. Ref. Data* 26 (1997) 1329-1499.
- [18] S. P. Sander, R. R. Friedl, D. M. Golden, M. J. Kurylo, R. E. Huie, V. L. Orkin, G. K. Moortgat, A. R. Ravishankara, C. E. Kolb, M. J. Molina, B. J. Finlayson-Pitts, *NASA Panel for Data Evaluation, Evaluation Number 14, JPL Publication 02-25, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, 2003.*
- [19] S. Dóbbé, T. Bérces, F. Márta, *Int. J. Chem. Kinet.* 18 (1986) 329-344.
- [20] R. Atkinson, E. S. C. Kwok, J. Arey, S. M. Aschmann, *Faraday Discuss.* 100 (1995) 23-37.
- [21] R. Atkinson, *Int. J. Chem. Kinet.* 29 (1997) 99-111.