

Study of NO₃ Radical Reactions with Oxygenated Organic Compounds in Aqueous Solution

Motivation and background

Free radicals such as NO₃ play an important role in the chemistry of the aqueous tropospheric phase. In order to understand the impact of free radical chemistry in the tropospheric aqueous phase kinetic data with relevant organic compounds are required. Oxygenated organic compounds are either directly emitted to the atmosphere as fuel additives or solvents or they are formed in the troposphere as intermediate products of chemical degradation of other volatile organic compounds. NO₃-radicals react with these oxygenated organic compounds mainly during nighttime via different reaction mechanisms. In this study already existing kinetic data have been supplemented and compared with rate constants for atmospheric relevant carbonyl compounds, carboxylic acids and their anions. Correlation among chemically similar compounds gives insight into the reaction mechanism involved and may also allow the prediction of unknown rate constants. Furthermore, kinetic data are essential for tropospheric chemical modeling.

Experimental

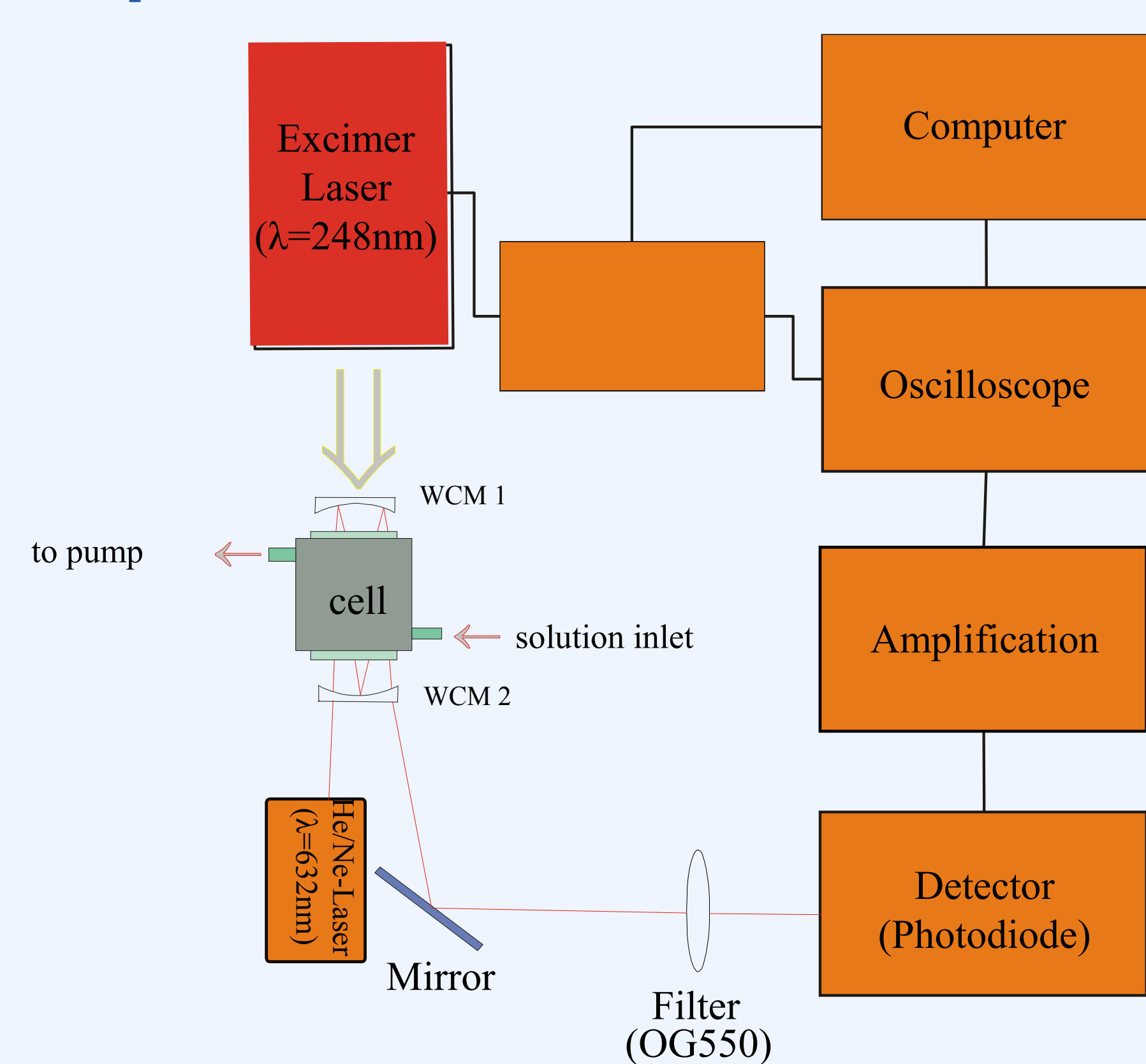
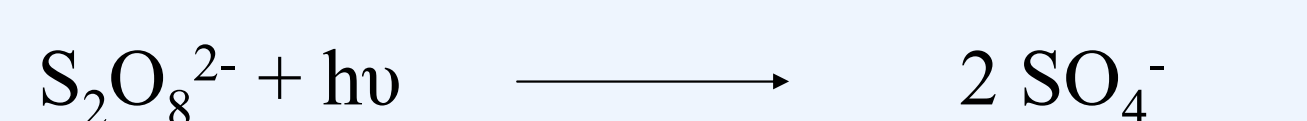


Figure 1: Experimental set-up of laser photolysis long path absorption (LP-LPA) experiment

Two different sources were used to generate NO₃-radicals via laser flash photolysis. Nitrate anions were photolysed at a wavelength of $\lambda = 248$ nm at pH = 0.5 adjusted with HClO₄. NO₃-radicals are produced via the following reactions:



A very low pH of 0.5 was necessary to have undissociated HNO₃ for the latter reaction to take place. For measurements at higher pH, peroxydisulfate ions (S₂O₈²⁻) were photolysed at a wavelength of $\lambda = 351$ nm, yielding sulfate radical anions that react with nitrate to form NO₃-radicals:



A laser photolysis long path laser absorption set-up (LP-LPA) was used for the kinetic investigations. The temporal decline of the NO₃ concentration caused by reaction with the organic reactant was observed using a He-Ne laser operated at the NO₃ absorption maximum of $\lambda = 632.8$ nm.

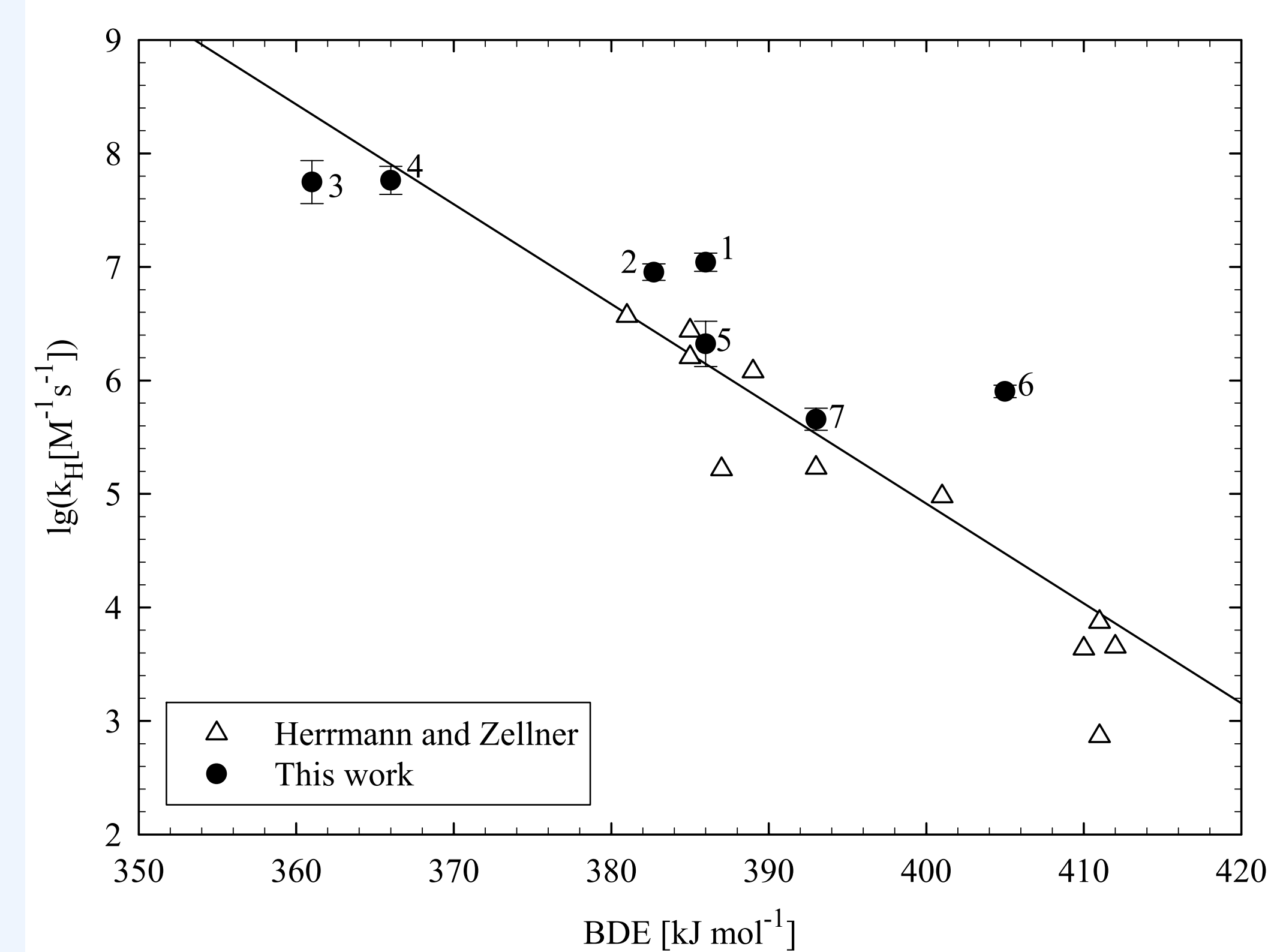


Figure 3: Plot of logarithm of the measured and literature rate constants [3] at 298 K per abstractable H-atom against the BDE.

In contrast to Figure 3 the plot of the E_A versus the BDE (see Fig.4) for the measured compounds and such from literature the data appears to be more scattered. Overall it could be said that the E_A increases with BDE for some compounds but without any straight correlation. From the data currently available exact reasons cannot be derived.

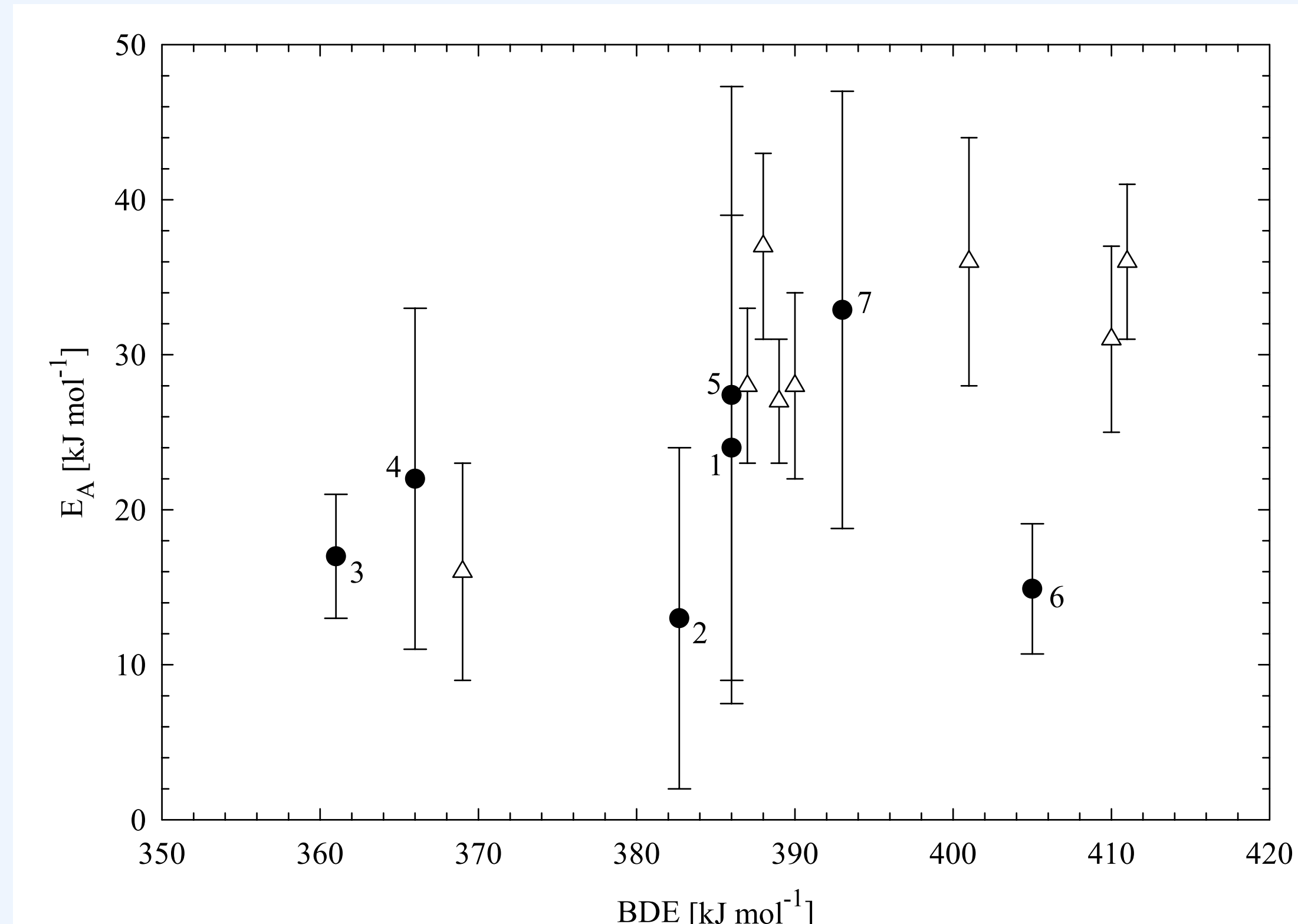


Figure 4: Plot of measurement obtained E_A and literature values [4] versus bond dissociation energy.

Results and discussion

Temperature dependent rate constants were measured for 4 carbonyl compounds, 3 carboxylic acids and their anions (Table 1). Much faster rate constants measured for the anions in comparison with the acids suggest a different reaction mechanism. From the Arrhenius equation, the Activation Energy (E_A) and the preexponential factor (A) were obtained. The Arrhenius plots for the aldehydes are shown in Figure 2.

Table 1: Observed rate constants at 298K, Arrhenius preexponential factors and activation energy.

No	Compound	Formula	Equival. H-Atoms	BDE [kJ mol ⁻¹]	A [s ⁻¹]	E_A [kJ mol ⁻¹]	$k_{2nd, 298}$ [M ⁻¹ s ⁻¹]	NO ₃ source
1	2-Butanone	C ₂ H ₅ C(O)CH ₃	2	*386	(4 ± 0.9) · 10 ¹¹	24 ± 15	(2.2 ± 0.4) · 10 ⁷	a
2	Hydroxyacetone	CH ₃ C(O)CH ₂ OH	2	*382.7	(4 ± 0.8) · 10 ⁹	13 ± 11	(1.8 ± 0.3) · 10 ⁷	a
3	Butyraldehyde	C ₃ H ₇ CHO	1	*361	(5 ± 0.4) · 10 ¹⁰	17 ± 4	(5.6 ± 2.3) · 10 ⁷	a
4	Propionaldehyde	C ₂ H ₅ CHO	1	*366	(3 ± 0.5) · 10 ¹¹	22 ± 11	(5.8 ± 1.6) · 10 ⁷	a
5	Lactic acid	CH ₃ CH(OH)COOH	1	#386	(1.0 ± 0.3) · 10 ¹¹	27.4 ± 19.9	(2.1 ± 0.9) · 10 ⁶	b
6	Pyruvic acid	CH ₃ C(O)COOH	3	*405	(9.6 ± 0.8) · 10 ⁸	14.9 ± 4.2	(2.4 ± 0.3) · 10 ⁶	b
7	Glycolic acid	CH ₂ OHCOOH	2	*393	(4.5 ± 0.9) · 10 ¹¹	32.9 ± 14.1	(9.1 ± 0.2) · 10 ⁵	b
8	Lactate	CH ₃ CH(OH)COO ⁻			(8.3 ± 0.4) · 10 ¹⁰	22.5 ± 2.8	(1.0 ± 0.2) · 10 ⁷	b
9	Pyruvate	CH ₃ C(O)COO ⁻			(3.7 ± 0.3) · 10 ¹¹	24.3 ± 5.0	(1.9 ± 0.5) · 10 ⁷	b
10	Glycolate	CH ₂ OHCOO ⁻			(1.8 ± 0.2) · 10 ¹¹	24.5 ± 8.9	(1.0 ± 0.2) · 10 ⁷	b

a Nitrate photolysis *calculated after [1]

b Peroxydisulfate photolysis #from [2]

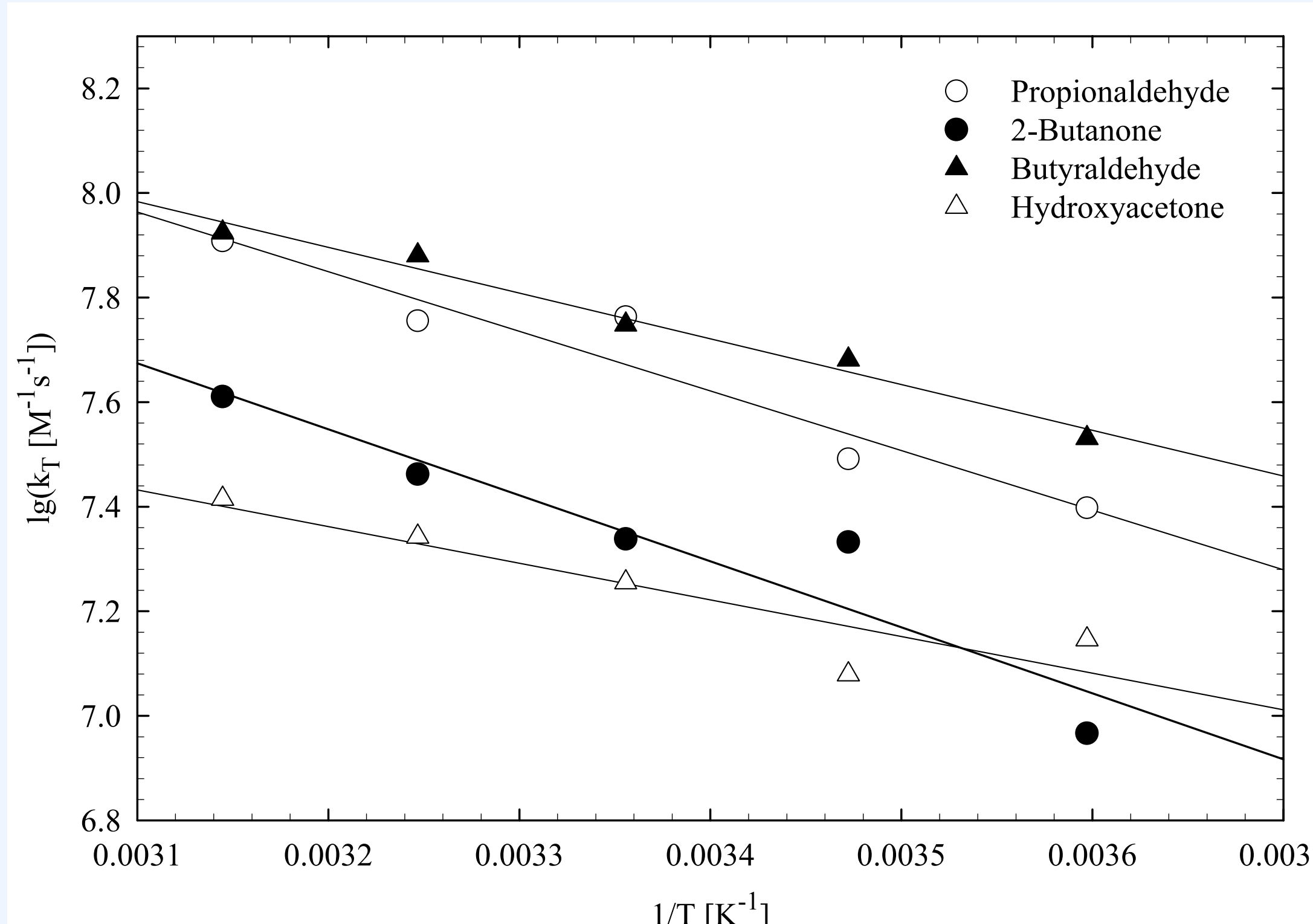


Figure 2: Arrhenius plot for Propionaldehyde, 2-Butanone, Butyraldehyde and Hydroxyacetone

For both the activation energy (E_A) and the logarithm of the rate constant of an H-abstraction reaction a linear dependence on the C-H bond energy is presumed. The bond energy of the weakest C-H bond, which is most likely to be broken in an H-abstraction reaction, is referred to as bond dissociation energy (BDE) [3]. The measured rate constants divided by the number of the equivalent abstractable H-atoms were plotted against the BDE (Fig.3). These data were supplemented by literature rate constants [3] and BDEs of other aliphatic compounds yielding the following correlation line:

$$\lg(k/nH) = (40.1 \pm 7.7) - (0.088 \pm 0.020) \cdot \text{BDE}$$

$$R=0.91 \text{ and } n=18 \text{ k [M}^{-1}\text{s}^{-1}\text{] ; BDE [kJ mol}^{-1}\text{].}$$

Conclusions

The measured compounds follow a correlation which suggests an H-abstraction reaction with NO₃. This correlation might be used for a good approximation of unknown rate constants of H-atom abstraction reactions, if the BDE of the particular compound is well known. But it should be always critically applied especially if contribution from other reaction mechanisms is likely.

References

- [1] S.W. Benson *Thermochemical Kinetics*, Wiley: New York, 1976
- [2] V.E. Tumanov et al., *Russ. Chem. Bull.*, 2002, 51, 1641
- [3] H. Herrmann and R. Zellner in Alfassi, *N-centered radicals*, Wiley: New York, 1998, 291
- [4] H. Herrmann *Habilitation*, Essen, 1997