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Science and Technology
Doctoral School of Science of Matter,
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Field: Optics and lasers, physical chemistry, atmosphere

University of Szeged
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Atmospheric kinetics and photochemistry of oxygenated volatile organic compounds

Summary of PhD Thesis

by

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1. Introduction

Oxygenated volatile organic compounds (OVOCs) are important constituents of the atmosphere. They include, e.g., aliphatic alcohols, aldehydes, ketones, and organic acids. In the free troposphere, the abundance of OVOCs is higher than that of the non-methane hydrocarbons and their overall reactivity with OH is comparable with that of methane, in contrast that methane is present in much higher concentration. Degradation of OVOCs in the atmosphere takes place via the reaction with OH radicals and, in the case of photochemically active molecules, via photolysis. Free radicals are formed in the photooxidative degradations of the oxygen-containing organics which basically determine the oxidative capacity of the atmosphere, the transformation of nitrogen oxides and the concentration of OH radicals and tropospheric ozone. Ozone is the third most important greenhouse gas in the atmosphere, it is one of the toxic components of urban smog and so it is related to such grave environmental problems as global warming and the quality of air. OVOCs have both natural and anthropogenic sources (vegetation, industry, traffic) and are formed in a great part via the oxidation of hydrocarbons in the atmosphere.

All organics that I have selected for reaction kinetics and photochemical studies contain the carbonyl, C=O, group. The presence of a carbonyl group significantly affects the reactivity leading to reduced or even increased reactivity toward OH radicals depending on the position of the carbonyl group and other substituents in the molecules. Characteristic for several of the carbonyl molecules is that they absorb light and undergo photochemical reactions at relatively long wavelengths, already in the actinic region (λ > 290 nm), thus they are photochemically active in the troposphere.

The following reactions are subjects of my PhD work:

$OH + CH_3C(O)OH$ (d_0-AA) → products $\quad k_1 \quad$ (1)

$OH + CH_3C(O)OD$ (d_1-AA) → products $\quad k_2 \quad$ (2)

$OH + CD_3C(O)OH$ (d_3-AA) → products $\quad k_3 \quad$ (3)

$OH + CD_3C(O)OD$ (d_4-AA) → products $\quad k_4 \quad$ (4)

$OH + CH_3C(O)CH_2CH_3$ (MEK) → products $\quad k_5 \quad$ (5)

$CH_3C(O)C(O)CH_2CH_3$ (2,3PD) + $h\nu$ → products $\quad \sigma_{2,3PD}, J_{2,3PD}, \Phi_{2,3PD} \quad$ (6)

$OH + CH_3C(O)C(O)CH_2CH_3$ (2,3PD) → products $\quad k_7 \quad$ (7)

$HOCH_2CHO$ (GA) + $h\nu$ → products $\quad J_{GA} \quad$ (8)

Reaction rate constants, k_1-k_5 and k_7, photolysis quantum yields, $\Phi_{2,3PD}$, and photolysis rate constants, $J_{2,3PD}$ and J_{GA} were determined. Absorption cross sections of 2,3PD, $\sigma_{2,3PD}$, as a function of wavelength (λ) were also measured. Determination of rate constants for the OH reactions allowed to assess reactivity – molecular structure relationships and to estimate the atmospheric lifetimes of the studied OVOCs with respect to their OH reactions. The determined photochemical parameters have provided insight into the photochemistry of carbonyl molecules in general, and allowed to estimate the photolysis lifetime of the studied photochemically active organics. Both the determined reaction kinetic and photochemical data can be used as input parameters for atmospheric modelling studies.

I have done my PhD research in the framework of a French-Hungarian "Agreement Pursuant to a Co-Tutorial Thesis" signed between the University of Lille and the University of Szeged. The experiments were carried out both in France (Ecole des Mines de Douai) and in Hungary (Chemical Research Center, Budapest) by making use of the different experimental techniques that are available at the two research sites.

2. Experimental

I have carried out reaction kinetic and photochemical investigations applying several experimental techniques and procedures that are essentially complementary to each other.

The relative rate (RR) method was used to determine rate constants, for reaction (1) - (4) and (7). Application of the RR method involves the measurement of the rate of consumption of the studied reactant simultaneously with that of a reference compound, the rate constant for which is accurately known. In this way, rate constant ratios are obtained that are converted to absolute values by taking rate constants for the reference reactions from the literature. The experiments were carried out both in a ~ 250 L Teflon-bag reactor and a 10 L Pyrex bulb at atmospheric pressure in air using the photooxidation of methyl nitrite (CH_3ONO) as the source of OH radicals. The concentration depletion of the reactants and reference compounds were measured by gas-chromatographic (GC) analysis using flame ionisation detection (FID).

The direct discharge flow (DF) method was applied to determine absolute rate constant for reactions (5) and (7). This technique allows the investigation of elementary reactions at the *ms* time scale by direct observation of atoms and free radicals. The main part of the kinetic apparatus is a flow reactor equipped with a movable injector. The OH radicals were produced inside the injector by reacting H atoms with NO_2; H atoms were obtained by microwave discharge. The reactants were highly diluted in He and were introduced through a side arm at the upper end of the reactor. The reaction time is set by the linear flow rate and the distance between the tip of the injector and the detection block. OH radicals were monitored at the end of the flow tube by using the sensitive and selective detection method of resonance fluorescence (RF). The RF lamp used for OH detection was a quartz tube operated by microwave discharge of flowing H_2O vapour in argon. The experiments were carried out under pseudo-first-order condition, that is, in high excess of the reactants over [OH].

The absorption spectrum of 2,3PD, was determined by using a home-built single-path UV / Vis spectrophotometer. The measured absorbencies were converted to absorption cross section, $\sigma_{2,3\mathrm{PD}}(\lambda)$, by employing the Beer-Lambert law.

The photolysis rate constants, (‘photolysis frequencies’) of 2,3PD, $J_{2,3\mathrm{PD}}$, were determined in air, at 254 and 312 nm wavelengths in the Teflon-bag reactor using fluorescent lamps for irradiation. The consumption of 2,3PD was measured as a function of reaction time using GC-FID. The photolysis frequencies of 2,3PD were made independent of the photon fluxes by means of NO_2- and acetone actinometry. In this way, effective quantum yields, $\Phi^{\mathrm{eff}}_{2,3\mathrm{PD}}$, could be derived for the non-monochromatic light sources.

Determination of $\Phi_{2,3PD}$ with pulsed laser photolysis (PLP) was achieved by performing the irradiations with a XeF exciplex laser (λ = 351 nm) in a cylindrical quartz cell (QR). The reaction mixture, beside 2,3PD, contained a GC internal standard and air. Samples were taken at regular time intervals with a gas-tight syringe and the concentrations measured by the GC. The number of laser shots (the reaction time) was recorded and the laser energy per pulse was measured. The quantum yield was calculated by the concentration depletion of 2,3PD and the absorbed laser energy.

The error limits given in this Summary and throughout my Thesis designate 1σ statistical uncertainty, unless otherwise stated.

3. Results

3.1. OH reaction kinetics of acetic acid and deuterated acetic acids

Rate constant for the reactions of OH radicals with acetic acid (1) and its deuterated variants (2, 3, 4) have been determined by using the relative rate (RR) kinetic method. The experiments were performed in the Teflon-bag reactor (RR-TR experiments) at $T = 300 \pm 2$ K in atmospheric pressure air. In the relative-rate measurements rate constant ratios are determined by comparing the rate of loss of the substrate studied to that of the reference compounds, the rate constant of which is known or determined by independent direct kinetic studies. Specifically for the reaction of OH with acetic acid, the following reaction competition was applied:

$$\mathrm{OH} + \mathrm{CH_3C(O)OH}\ (d_0\text{-AA}) \rightarrow \text{products (1) (studied reaction)}$$

$$\mathrm{OH} + \mathrm{CH_3OH} \rightarrow \text{products (22) (reference reaction)}$$

Provided that neither the substrate d_0-AA, nor the reference CH_3OH are lost by reactions other than (1) and (22) and they are not reformed in the reaction system, the following expression is obtained by integration:

$$\ln\{[d_0\text{-AA}]_0 / [d_0\text{-AA}]_t\} = (k_1 / k_{22}) \times \ln\{[\mathrm{CH_3OH}]_0 / [\mathrm{CH_3OH}]_t\} \qquad \text{(Eq. 1)}$$

where $[d_0\text{-AA}]_0$, $[d_0\text{-AA}]_t$, $[\mathrm{CH_3OH}]_0$, and $[\mathrm{CH_3OH}]_t$ are the concentrations at time zero and *t*, respectively. The following reference reactants were used for the other acetic acid reactions: OH + d_1-AA (2): CD_3OD, OH + d_3-AA (3): CH_3OH, OH + d_4-AA (4): CD_3OD.

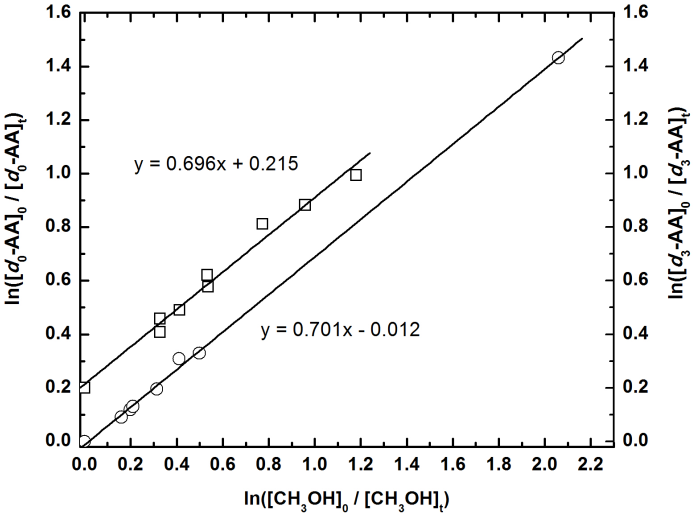

Figure 1: Typical relative rate plots. Squares: d_0-AA ($CH_3C(O)OH$), circles: d_3-AA ($CD_3C(O)OH$). The data for $CH_3C(O)OH$ have been shifted by 0.2 for clarity. The rate constant ratios k_1 / k_{22} and k_3 / k_{22} have been obtained as the slopes of the straight lines.

The determined rate constant ratios have been converted to absolute values by taking the rate constant of the reference reactions from the literature. The following results have been obtained: k_1(OH + d_0-*AA*) = (6.3 ± 0.9), k_2(OH + d_1-*AA*) = (1.5 ± 0.3), k_3(OH + d_3-*AA*) = (6.3 ± 0.9) and k_4(OH + d_4-*AA*) = (0.90 ± 0.1) all given in 10^{-13} cm^3 $molecule^{-1}$ s^{-1} ($T = 300 \pm 2$ K).

3.2. OH reaction kinetics of methyl-ethyl-ketone

The reaction OH + MEK (5) was studied by using the direct DF-RF method ($T = 297 \pm 3$ K, $p = 3.17 \pm 0.08$ mbar He). The experiments were carried out under pseudo-first-order conditions with high excess of methyl-ethyl-ketone concentration over that of OH, $[MEK] >> [OH]_0$. In this way, due to the high sensitivity and selectivity of OH detection, reaction (5) could be studied essentially in isolation from the interferring parallel and consecutive reactions. Under the plug-flow conditions of the fast DF technique, the reaction time is given simply as the ratio of the varied reaction distance and the linear flow rate, $t = z / \bar{v}$. Accordingly, the experimental observables were evaluated by equations (2 - 4):

$$-\ln(S_{\mathrm{on}}^{\mathrm{OH}} / S_{\mathrm{off}}^{\mathrm{OH}}) = k_5^{'} \, (z / \bar{v}) \qquad \text{(Eq. 2)}$$

$$k_5^{'} = k_5 \; [\mathrm{CH_3C(O)CH_2CH_3}] + \mathit{const.} \qquad \text{(Eq. 3)}$$

$$-\ln S_{\mathrm{off}}^{\mathrm{OH}} = k_{\mathrm{w}} \, (z / \bar{v}) \qquad \text{(Eq. 4)}$$

where $S_{\mathrm{on}}^{\mathrm{OH}}$ and $S_{\mathrm{off}}^{\mathrm{OH}}$ are the amplitudes of the OH RF signals in the presence and absence of MEK, respectively. k_5’ is the pseudo-first-order rate constant. Even under the applied pseudo-first-order conditions the heterogeneous loss of OH took place, the rate constant of which, k_{w}, could be determined in the absence of MEK according to Eq. 4.

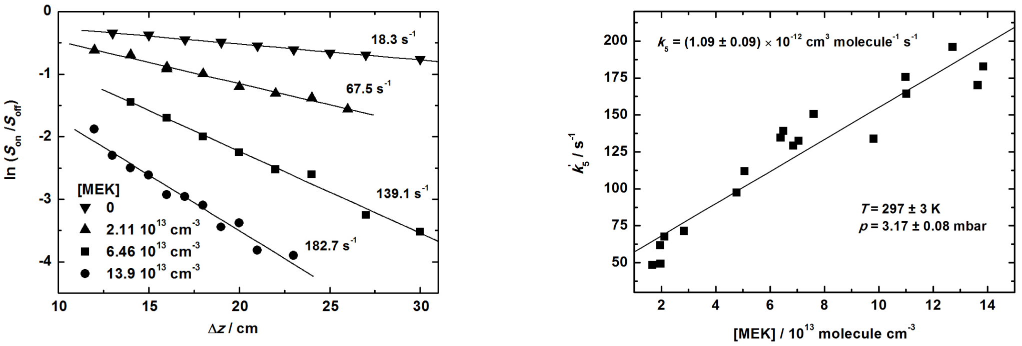

Figure 2: DF-RF kinetic plots used to obtain rate constant for the reaction OH + MEK (5). On the left hand side, typical semi-logarithmic OH decays are presented (cf. Eq. 2). The pseudo-first-order plot on the right hand side provides k_5, as slope of the straight line (cf. Eq. 3).

The following rate constant has been proposed by the DF-RF investigation:

$$k_5 \text{ (297 K)} = (1.09 \pm 0.09) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

The reaction of MEK with OH, together with the rate constant that I have determined by the direct DF method, have been utilized in relative-rate studies of the OH + 2,3PD (7) reaction (see below).

3.3. Reaction kinetic and photochemical study of 2,3-pentanedione

The most detailed investigations have been performed with 2,3PD, which belongs to the important family of α-dicarbonyls. OH reaction rate constants (k_7), absorption cross sections ($\sigma_{2,3\mathrm{PD}}$), photolysis frequencies ($J_{2,3\mathrm{PD}}$) and quantum yields ($\Phi_{2,3\mathrm{PD}}$) were determined.

OH reaction kinetics. Both direct (DF-RF) and relative rate (RR) experimental techniques were used to determine the rate constant for the overall reaction OH + 2,3 PD (7).

The DF-RF experiments were carried out at T = 300 ± 3 K reaction temperature and p = 2.49 ± 0.03 mbar He pressure. The experiments were conducted and the evaluations were carried out by using the usual pseudo-first-order conditions and evaluation scheme (Section 3.2). Consumption of OH on the walls of the reactor was somewhat higher than usual in DF experiments, but the pseudo-first-order plots provided good straight lines. The following rate constant was determined in the DF-RF study: $k_7(300\ \mathrm{K}) = (2.25 \pm 0.12) \times 10^{-12}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$, given with 1σ statistical uncertainty.

The RR studies were carried out both in the collapsible Teflon-bag reactor (RR-TR experiments) and the Pyrex reactor (RR-PR experiments) at T = 300 ± 2 K, and T = 302 ± 4 K, respectively, in atmospheric pressure synthetic air. 2,3PD was found to photolyse slowly at the wavelengths used to produce the OH radicals (362 and 365 nm). The significance of photolysis was quantified by separate experiments in the absence of the OH radical source, methyl nitrite, and was taken into account as minor correction in the RR kinetic equations (Eq. 1). The following reference reactions were used: RR-TR, OH + MEK (5) and OH + C_2H_5OH (24); RR-PR, OH + MEK (5). The RR plots, similar to those shown in Figure 1, have obeyed straight lines providing rate constants relative to the reference reactions. The k-ratios were put on the absolute scale by taking evaluated kinetic data form the literature with the results of k_7 = (1.95 ± 0.17), (2.50 ± 0.23) (RR-TR) and (2.06 ± 0.17) (RR-PR) given in $10^{-12}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$.

The good agreement lends credence to the reliability of the results that were obtained from independent measurements using different experimental techniques. The recommended rate constant for the reaction of OH radicals with 2,3PD is the non-weighted average of the k_7 determinations (the error is the estimated overall uncertainty proposed as 1σ):

$$k_7(300\ \mathrm{K}) = (2.19 \pm 0.22) \times 10^{-12}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}.$$

Photochemical study of 2,3PD. As a first step, the absorption spectrum of 2,3PD was determined: the wavelength dependent cross sections, $\sigma_{2,3PD}(\lambda)$, were obtained from absorption measurements using the home-constructed gas spectrophotometer and evaluating the data by the Beer-Lambert law.

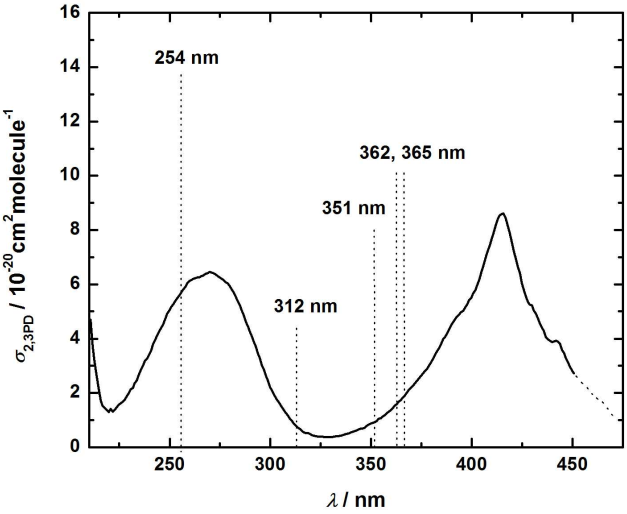

Figure 3: Absorption spectrum of 2,3PD in the gas phase. Designated are also the wavelengths where the photochemical and kinetic experiments were carried out.

Photolysis studies of 2,3PD were carried out by employing pulsed laser photolysis (PLP-QR) at λ = 351 nm and also stationer photolysis (SP-TR) with fluorescent lamps emitting at λ = 254 and 312 nm wavelengths, in a quartz cylindrical cell and the collapsible Teflon chamber, respectively.

In the PLP-QR experiments the photolysis quantum yield (QY), $\Phi_{2,3PD}$(351 nm), was determined (T = 300 ± 2 K, p = 1000 mbar air). The concentration of 2,3PD was measured by GC analysis before photolysis, $[2,3PD]_0$, and after n laser shots, $[2,3PD]_n$. QY was obtained by applying equation 5:

$$\ln([2,3PD]_n / [2,3PD]_0) = -\ C \times \Phi_{2,3PD}(351\ \text{nm}) \times (n \times E) \qquad \text{(Eq. 5)}$$

where E is the laser energy per pulse and C is a constant containing known parameters such as the optical path length, $\sigma_{2,3PD}(\lambda)$, etc. A plot of $\ln([2,3PD]_n / [2,3PD]_0)$ versus $n \times E$ has provided a straight line, and the photolysis quantum yield of $\Phi_{2,3PD}$(351 nm) = 0.11 ± 0.01 was obtained from the slope (Eq. 5).

In the SP-TR continuous-photolysis experiments performed with fluorescent lamps, the photolysis rate constants ("photolysis frequencies") were determined. The concentration depletion of 2,3PD was found of single-exponential by GC measurements providing the photolysis rate constants as decay constants: $J_{2,3PD}$ (254 nm) = 4.60 ± 0.09 and $J_{2,3PD}$ (312 nm) = 1.40 ± 0.03, all in 10^{-5} s^{-1}. The photolysis rate constants have been normalized for the different photon fluxes by using NO_2- or acetone actinometry. The $J_{2,3PD}$ values normalized to the actinometry photolysis frequencies were used to determine an "integral" or "effective" quantum yield, $\Phi_{2,3PD}^{eff}$, for the photolysis of 2,3PD by taking into account the emission spectra of the fluorescent lamps.

Table 1. Summary of photolysis quantum yields for 2,3-pentanedione

$\boldsymbol{\Phi_{2,3PD}^{eff}}$ **(254 nm)**[a]	$\boldsymbol{\Phi_{2,3PD}^{eff}}$ **(312 nm)**[b]	$\boldsymbol{\Phi_{2,3PD}}$ **(351 nm)**
0.29 ± 0.01	0.41 ± 0.02	0.11 ± 0.01

[a] Acetone actinometry. [b] NO_2 actinometry.

3.4. Photolysis study of glycolaldehyde

These experiments were performed in the Teflon-bag reactor at T = 300 ± 2 K, in atmospheric pressure air using 312 nm fluorescent tubes for irradiation; only a few experiments were carried out.

The consumption of glycolaldehyde, (GA), was monitored as a function of reaction time using HPLC analysis. Single-exponential time behaviour was observed with the photolysis rate constant of $J_{GA}(300K) = (1.48 \pm 0.05) \times 10^{-4}\ s^{-1}$.

Formaldehyde and methanol were indentified as primary photolysis products, but their yields (Γ_{HCHO} and Γ_{CH3OH}) could be determined only with large uncertainty: Γ_{HCHO} = 10.4 – 26.7 % and Γ_{CH3OH} = 1.8 – 8.7 %.

4. New scientific results

1. The rate constant of k_5(297 K) = (1.09 ± 0.09) × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} has been determined for the reaction of OH radicals with methyl-ethyl-ketone (MEK) by using the direct, low-pressure, fast discharge flow (DF) technique coupled with resonance fluorescence (RF) detection of OH [1]. This is the first rate constant for reaction (5) determined with the thermal DF-RF method: previous experiments applied photolytic techniques. Conversely, the obtained k_5 value is in good agreement with the literature recommendations, thus it has become one of the best known kinetic parameters.

2. Relative rate (RR) experiments were carried out in a Teflon chamber to determine rate constants for the reactions: OH + $CH_3C(O)OH$ (d_0-AA) (1), OH + $CH_3C(O)OD$ (d_1-AA) (2), OH + $CD_3C(O)OH$ (d_3-AA) (3), and OH + $CD_3C(O)OD$ (d_4-AA) (4) [2]. While, the rate constants k_1, k_3, and k_4 agree well with most of the literature data, the measured k_2(OH + d_1-*AA*) = (1.5 ± 0.3) × 10^{-13} cm^3 $molecule^{-1}$ s^{-1} is the first kinetic result for reaction (2). The rate constants display characteristic differences depending on the site of the D-substitution in the molecules: $k_1 \approx k_3 >> k_4$ and $k_2 \geq k_4$ (T = 300 K). These results show a significant primary deuterium isotope effect, and confirm that it is the acidic H-atom which is abstracted preferentially in the reaction of OH with acetic acid. It is contrary that the O-H bond has higher dissociation energy compared with that of the (H_2)C-H bond. By the kinetic results of the current work, the group rate constant of k_{CD3} = 1.13 × 10^{-13} cm^3 $molecule^{-1}$ s^{-1} is proposed for use in the estimations of OH reaction rate constants.

3. Rate constant for the reaction OH + $CH_3C(O)C(O)CH_2CH_3$ (2,3PD) (7) has been determined the first time. Both relative and direct kinetic measurements of k_7 were carried out. Altogether 4 types of experiments were performed at two research sites, comprising the wide pressure range of ~ 2 mbar and ~ 1000 mbar. The RR and DF kinetic studies have provided rate constants in good agreement with each other: the proposed average value is k_7(300 K) = (2.19 ± 0.22) × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. The determined k_7 implies significant enhanced reactivity. The relatively high rate constant is attributed to the presence of the CH_2 group in β-position to one of the carbonyl groups in the 2,3PD molecule. To account for the activating effect of vicinal carbonyl groups, the F(–C(O)C(O)-) = 1.55 value is recommended for use in group additivity estimations of OH reaction rate constants [4].

4. The gas phase absorption spectrum of 2,3PD has been determined to extend well into the visible region. It is characterized by two wide absorption bands resembling the spectrum of the lower homolog α-diketone, 2,3-butanedione (biacetyl) [4].

5. Pulsed laser photolysis (PLP, 351 nm) and continuous photolysis (SP, 254, 312 nm) were applied to determine quantum yields (QY), ($\Phi_{2,3PD}$) for 2,3-pentanedione. Surprisingly high QYs were obtained at the longer wavelengths, but only in poor agreement with each other [4]. The average value of $\Phi_{2,3PD} \approx 0.3$ is proposed over the wavelength range ~ 310 – 360 nm. All three wavelengths represent sufficient energy to initiate photodissociation processes via C-C bond rupture: the formation of acyl radicals have been validated by product studies. No gas-phase photochemical study of 2,3PD has been reported previously.

6. The determined reaction rate constants and photochemical parameters allow the estimation of the tropospheric lifetimes of the studied molecules. The following lifetimes are estimated with respect to the OH reactions: τ_{OH}(acetic acid) = 18 days, τ_{OH}(MEK) = 11 days, and τ_{OH}(2,3PD) = 5.3 days. Although the exact value is still quite uncertain, it is proposed that atmospheric removal of 2,3PD occurs predominantly through photolysis with the short tropospheric lifetime of τ_{phot}(2,3PD) < 1 hour [4].

5. List of scientific publications

Publications

1. Direct kinetic study of the reaction of OH radicals with methyl-ethyl-ketone
E. Szabó, G. L. Zügner, I. Szilágyi, S. Dóbé, T. Bérces, F. Márta
React. Kinet. Catal. Letters, 95, 365-371, (2008); if.: 0.610.

2. Kinetics of the OH-radical initiated reactions of acetic acid and its deuterated isomers
E. Szabó, J. Tarmoul, A. Tomas, C. Fittschen, S. Dóbé, P. Coddeville
React. Kinet. Catal. Letters, 96, 299–309, (2009); if.: 0.587.

3. OH yields for $C_2H_5CO + O_2$ at low pressure: experiment and theory
G. L. Zügner, I. Szilágyi, J. Zádor, E. Szabó, S. Dóbé, X. Song, B. Wang
Chem. Phys. Letters, 495, 179–181 (2010); if.: 2.291.

4. Atmospheric chemistry of 2,3-pentanedione: photolysis and reactions with OH radicals
E. Szabó, M. Djehiche, M. Riva, C. Fittschen, P. Coddeville, D. Sarzyński, A. Tomas, S. Dóbé
J. Phys. Chem. A, 115, 9160-9168, (2011); if.: 2.899.

5. Direct kinetic study of the OH-radical initiated oxidation of pivalaldehyde, $(CH_3)_3CC(O)H$, in the gas phase
E. Szabó, G. L. Zügner, M. Farkas, I. Szilágyi, S. Dóbé
Oxidation Communications, (submitted: 09. 05. 2011); if.: 0.240.

Total sum of impact factors: **6.627**

Presentations

1. Degradation of acetic acid in an atmospheric simulation chamber, Szabó Emese, *"Modern Techniques in Atmospheric Physics and Chemistry"* meeting, Szeged, Hungary, 2-4 May 2007. (oral presentation)

2. Oxydation de l'acide acétique et de ses isotopes deutérés par le radical OH, Emese Szabó, A. Tomas, P. Coddeville, C. Fittschen, S. Dóbé, *Journée des doctorants de PC2A*, Lille, France, 11 January 2008. (oral presentation)

3. Photolyse du benzène à 254 nm en chambre de simulation atmosphérique, Szabó Emese, *Conférence annuelle de Cinétique et de Photochimie*, Strasbourg, France,
9-10 June 2008. (oral presentation)

4. Oxigéntartalmú molekulák légköri lebomlásának vizsgálata szmog-kamrában, Szabó Emese, *XII. Doktori Kémiai Iskola*, Gyöngyöspata, Hungary, 20-21 April 2009. (oral presentation)

5. Az ecetsav és a 2,3-pentándion légkörkémiai kinetikájának és fotokémiájának vizsgálata szmog-kamra kísérletekkel, Szabó Emese, *MTA Reakciókinetikai és fotokémiai munkabizottsági ülése,* Balatonalmádi, Hungary, 23-24 April 2009. (oral presentation)

6. A 2,3-pentándion reakciókinetikai és fotokémiai vizsgálata szmog-kamra kísérletekkel és direkt kísérleti módszerekkel, Szabó Emese, *MTA Kutatóközponti Tudományos Napok*, Budapest, Hungary, 24-26 November 2009. (oral presentation)

7. OH reaction rate constant and photolysis quantum yield for 2,3-pentanedione, Szabó Emese, *Hungarian-Polish research group meeting*, Wroclaw, Poland, 5-9 December 2009. (oral presentation)

8. A γ-valerolakton és a hidroxilgyök gázfázisú elemi reakciójának kinetikai vizsgálata, Farkas Mária, Zügner Gábor László, Szabó Emese, Zsibrita Dóra, Dóbé Sándor, *MTA Reakciókinetikai és Fotokémiai Munkabizottság ülése,* Gyöngyöstarján, 2010. október 28-29, (oral presentation)

9. Oxydation de l’acide acétique et de ses isotopes deutérés par le radical OH dans une chambre de simulation atmosphérique, E. Szabó, J. Tarmoul, A. Tomas, C. Fittschen, P. Coddeville, S. Dóbé, *Journées Interdisciplinaires de la Qualité de l’Air*; Villeneuve d’Ascq, France, 7-8 February 2008. (poster)

10. Benzene photolysis at 254 nm in an atmospheric simulation chamber, E. Szabó, A. Tomas, C. Fittschen, P.Coddeville, *Marie-Curie EST Joint meeting*, Lille, France, June 2008. (poster)

11. Benzene photolysis at 254 nm: quantum yield and reaction products, E. Szabó, A. Tomas, C. Fittschen, P. Coddeville, R. Nádasdi, S. Dóbé, *20th International Symposium on Gas Kinetics*, Manchester, England, 20-25 July 2008. (poster)

12. Photolysis quantum yield and OH reaction rate constant for methyl-ethyl-ketone, R. Nádasdi, G. L. Zügner, I. Szilágyi, S. Dóbé, E. Szabó, A.Tomas and C. Fittschen, *20th International Symposium on Gas Kinetics*, Manchester, England, 20-25 July 2008. (poster)

13. Direct and relative rate kinetic study of the reaction of OH radicals with ethyl-fluoride, G. L. Zügner, M. Farkas, E. Szabó, and S. Dóbé, *Doktoráns Konferencia,* BME, Budapest, Hungary, 4 February 2010. (poster)

14. Direct and Relative-Rate Kinetic Study of the Reaction OH + C_2H_5F, G. L. Zügner, M. Farkas, E. Szabó, D. Zsibrita, and S. Dóbé, *21th International Symposium on Gas Kinetics*, Leuven, Belgium, 18-23 July 2010. (poster)

15. Kinetic and Photochemical Study on the Atmospheric Fate of 2,3-Pentanedione, E. Szabó, D. Sarzynski, A. Tomas, P. Coddeville, C. Fittschen, and S. Dóbé, *21th International Symposium on Gas Kinetics*, Leuven, Belgium, 18-23 July 2010. (poster)

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Declarations

We, undersigned, co-authors of the publications, of *Ms. Emese Szabó* acknowledge with pleasure that she has had the most important contribution to the papers in which she is the first author and agree that the results be included in her PhD Thesis.

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Prof. Dr. Sándor Dóbé	Ms. Mária Farkas
……………………………...	……...
Dr. István Szilágyi	Mr. Gábor László Zügner

Budapest, May 12, 2011.

On the request of *Ms. Emese Szabó*, I assert that the new scientific results included in her PhD Thesis have not been and will not be utilized in other PhD work under my thesis supervision.

……………………………………
Prof. Dr. Sándor Dóbé
Thesis Supervisor of Ms. Emese Szabó

Budapest, May 12, 2011.