

Theses of Doctoral (PhD) Dissertation

**THE REACTIONS OF
1,4-BENZOQUINONES
WITH LIGHT AND SULFUR(IV)**

Virág Kiss

Dissertation supervisor: Dr. Katalin Ósz



UNIVERSITY OF DEBRECEN

Chemistry Doctoral School

Debrecen, 2018

Abbreviations

A_1, A_2	reactants
a_1	scaled concentration of A_1
a_2	scaled concentration of A_2
b	scaled concentration of I
c	scaled concentration of P
I	intermediate
P	product
pH_{set}	set pH value
Q	1,4-benzoquinone
QCl	2-chloro-1,4-benzoquinone
QMe	2-methyl-1,4-benzoquinone
QMe ₂	2,6-dimethyl-1,4-benzoquinone
QR	1,4-benzoquinone derivative
QR-H ₂	hydroquinone derivative
QR-OH	hydroxy-quinone derivative
Q-2,6-Cl ₂	2,6-dichloro-1,4-benzoquinone
Q-2,5-Cl ₂	2,5-dichloro-1,4-benzoquinone
α	mole fraction of the hydroxy-quinone derivative in the product of the photoreaction ($[\text{QR-OH}]/([\text{QR-OH}] + [\text{QR-H}_2])$)
$\epsilon_{\phi}^{\text{ini}}$	molar absorptivity of the quinone derivative at its excitation wavelength
$\epsilon_{\phi}^{\text{fin}}$	weighted average of the molar absorptivities of the photoproducts (QR-H ₂ , QR-OH) at the excitation wavelength
Φ	quantum yield
$\Phi_{\text{QR-OH}}$	quantum yield of the hydroxy-quinone derivative
Φ_p	photon flux of the UV lamp at the excitation wavelength
κ	scaled rate coefficient
κ_1^m, κ_2^m	measured and fitted (with double exponential function) pseudo-first order rate coefficients
ξ	reaction coordinate
l	optical path length
σ	initial concentration ratio of the reactants

Introduction and objectives

Currently, an essential problem of the society is the depletion of fossil fuels [1–3]. It is of great importance to utilize renewable energy sources to provide the energy demands of humanity [4]. Solar energy can be an attractive alternative, which takes advantage of the electromagnetic radiation continuously provided by the sun [5,6].

The aim of my study was to develop a method for the investigation of photochemical reactions, which enables rapid and fast determination of the quantum yield of the studied reaction [7]. It was required to develop this method without the use of special photochemical apparatus, and this method should also make the quantitative characterization of the reaction possible even when low light intensities are applied. Thus, it can be decided easily whether the given substance might be applicable for solar energy utilization or not. Quinone - a substance participating in photosynthesis - and its derivatives were selected for the development of this method [7].

It is an interesting problem that halobenzoquinones and their derivatives can promote cancer [8,9]. The number of cancer patients increases exponentially [10], discovering its sources and making them safe is essential. Therefore, another goal of my research was to find a way of the transformation of halobenzoquinones and their derivatives. For this reason, the ketone-bisulfite reaction was used. The detailed kinetic characterization of this reaction was desirable during my study.

Methods and instruments

A special pH-stat technique was applied for the studying the photochemical reactions of 1,4-benzoquinone (**Q**) and its derivatives (**Q-2,6-Cl₂**, **Q-2,5-Cl₂**, **QCl**, **QMe**, **QMe₂**) at different pH values (pH_{set}). The hydroxy-quinone derivatives (**QR-OH**) formed in the photoreaction of 1,4-benzoquinone derivatives (**QR**) are weak acids. Once the pH is set constant during the measurement, the formation of **QR-OH** can be followed easily by plotting the volume of the added base against the time. The schematic design of the pH-stat system is shown in Figure 1.

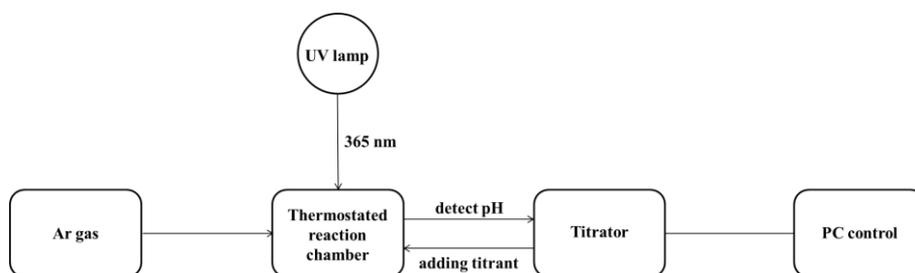


Figure 1: Schematic setup of the pH-stat apparatus [11]

The concentration change of hydrogen ion was followed with a Metrohm hydrogen ion selective glass electrode, which was connected to an ABU93 Triburette titrator. Initial pH values were set with KOH or H₂SO₄ solutions of known concentrations. The measurement was controlled by the stock software of the titrator, the pH and the volume of the continuously added KOH solution was measured in time. Spectroline FC-100/F UV-A lamp was used as a light source emitting at 365 nm wavelength. The photon flux of the lamp was determined with actinometry. During the pH-stat measurement the temperature was set constant (25.0±0.1 °C) with a Lauda K4R thermostat. Samples were stirred with

VWR Lab Disc magnetic stirrer and with a Teflon coated magnetic stir bar. Argon gas (99.996%, Linde) was bubbled through the samples to prevent the dissolution of carbon dioxide from the air into the samples.

It was verified with HPLC that the pH-stat technique is well applicable to study the photochemical reactions of **QR**. These analyses were carried out on a HP1090 liquid chromatographic instrument containing an autosampler and diode array detector. Separations were performed on a Hypersil ODS (100 × 4.6 mm, 3 μm) reversed phase column. Components were eluted under isocratic conditions (eluent: MeCN:0.1 v/v% trifluoroacetic acid = 18:82) and were detected at 200 and 280 nm. The flow rate of the eluent was 1 mL min⁻¹, the injected volume was 20 μL. The obtained data were evaluated with ChemStation software (Agilent, Santa Clara, CA).

During the examination of the reaction between **QR** and sulfur(IV), it was observed that 1,4-benzoquinones with electron withdrawing substituents (**Q-2,6-Cl₂**, **Q-2,5-Cl₂**, **QCl**) reacted very rapidly, on stopped-flow time scale. For fast kinetic measurements, an Applied Photophysics DX-17 MV sequential stopped-flow instrument was used. The temperature was set constant with a Julabo F12-ED thermostat to 25.0±0.1 °C. 99.99% nitrogen gas (Linde) was applied for the measurements. The Pro-Data SX v2.5.0 software was used for fast kinetic measurements. The dead time of the Applied Photophysics DX-17 MV Sequential stopped-flow instrument was 1.51±0.03 ms, which was determined with the reaction of 2,6-dichlorophenolindophenol and ascorbic acid, under ascorbic acid excess [12].

Kinetic fitting software were applied for matrix rank analyses, for determining p*K*_a values, for the evaluation of the kinetic curves of

photochemical reactions and also to evaluate measured and fitted curves obtained for the **QR**-sulfur(IV) reactions. MicroMath Scientist [13] was used for fitting with the least squares method. The ZiTa [14] kinetic fitting software was applied for fitting larger datasets. Matrix rank analyses were carried out with MatLab software [15].

New scientific results

1. For the first time, a pH-stat technique was used to follow the photoreactions of 1,4-benzoquinone derivatives to determine the quantum yield of the reaction.

It is well known that quinones are transformed into hydroxy- (**QR-OH**) and hydroquinone (**OR-H₂**) in a disproportion reaction, in the presence of light [16–18]. In my research, the photochemical reactions of 1,4-benzoquinones with electron donating (**QMe**, **QMe₂**) and electron withdrawing (**Q-2,6-Cl₂**, **Q-2,5-Cl₂**, **QCl**) substituents were studied in a wide pH range with the pH-stat technique [19].

An example kinetic curve recorded during the photochemical reaction is shown in Figure 2. During the measurement, the pH was set to 5.0, which was held constant by continuously adding KOH solution to the reaction (right side y axis). Furthermore, there was no change before turning the UV lamp on, after which a weak acid (**QR-OH**) was formed. The volume of the added KOH solution (V_{KOH}) was in proportion to the formation of this acid.

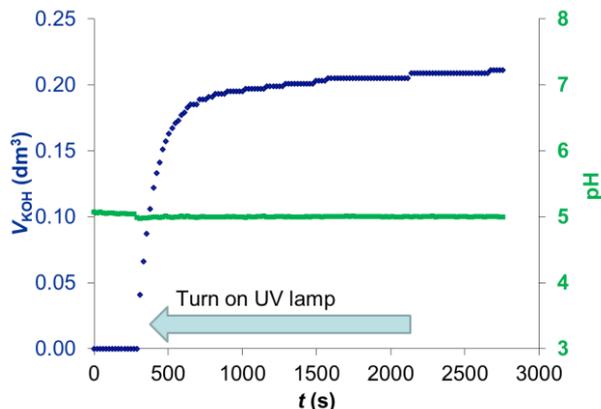


Figure 2: pH-Stat measurement of QMe

$$c(\text{QMe}) = 1.00 \cdot 10^{-3} \text{ M}, V(\text{QMe}) = 50.0 \text{ cm}^3$$

$$\text{pH}_{\text{set}} = 5.0, c(\text{KOH}) = 0.04147 \text{ M}, T = 298.2 \text{ K}$$

The optimal base and quinone concentrations, illumination time, set pH values were determined in the experiments and the quantum yield of the examined photoreaction was calculated based on these parameters.

2. An equation was created for the mathematical description of the kinetic curves obtained in the pH-stat measurements. This equation can be applied for any photochemical reaction that is accompanied with pH change, if the parameters are appropriately specified.

Most experiments were carried out in the pH range of $\text{p}K_{\text{a}}(\text{QR-OH}) + 1.5 < \text{pH}_{\text{set}} < \text{p}K_{\text{a}1}(\text{QR-H}_2) - 1.5$. With these initial parameters, the pH-stat kinetic curves describe the formation of the QR-OH, thus, $\Phi_{\text{QR-OH}}$ – the quantum yield of the formation of hydroxy-quinone derivative – can be expressed, as follows:

$$\Phi_{\text{QR-OH}} = \frac{dV_{\text{KOH}}}{dt} \frac{c_{\text{KOH}}}{\Phi_p (1 - 10^{-c_0 \ell \varepsilon_{\phi}^{\text{ini}}})} \quad (1)$$

where V_{KOH} is the volume of the added KOH solution, c_{KOH} is the exact concentration of the titrant, ℓ is the optical path length, $\varepsilon_{\phi}^{\text{ini}}$ is the molar absorptivity of the given **QR** at the excitation wavelength and Φ_p is the photon flux of the light source. With equation (1), only the first period (initial reaction rate) of the kinetic curves can be characterized. By taking into account the following two equations ((2) and (3)), too,

$$\frac{d\xi}{dt} = \frac{\Phi_p \Phi}{V_0 c_0} \left(1 - 10^{-\ell c_{\text{KOH}} c_0 ((1-\xi)\varepsilon_{\phi}^{\text{ini}} + \xi\varepsilon_{\phi}^{\text{fin}})/(c_{\text{KOH}} + \xi c_0)} \right) \frac{(1-\xi)\varepsilon_{\phi}^{\text{ini}}}{(1-\xi)\varepsilon_{\phi}^{\text{ini}} + \xi\varepsilon_{\phi}^{\text{fin}}} \quad (2)$$

$$V_{\text{KOH}} = \xi \alpha \frac{c_0 V_0}{c_{\text{KOH}}} \quad (3)$$

equation (4) is obtained, which can be used to fit entire kinetic curves. In equation (2), ξ is the reaction coordinate, V_0 is the initial volume of the sample (after setting the pH constant), $\varepsilon_{\phi}^{\text{fin}}$ is the weighted average of the molar absorptivities of the photoproducts (**QR-H₂**, **QR-OH**) at the excitation wavelength (365 nm) and c_0 is the initial concentrations of quinone solutions (**QR**).

$$\frac{dV_{\text{KOH}}}{dt} = \alpha \frac{\Phi_p \Phi}{c_{\text{KOH}}} \left(1 - 10^{-\ell (\alpha V_0 c_0 \varepsilon_{\phi}^{\text{ini}} + V_{\text{KOH}} c_{\text{KOH}} (\varepsilon_{\phi}^{\text{fin}} - \varepsilon_{\phi}^{\text{ini}})) / (V_{\text{KOH}} + \alpha V_0)} \right) \cdot \frac{(\alpha V_0 c_0 - V_{\text{KOH}} c_{\text{KOH}}) \varepsilon_{\phi}^{\text{ini}}}{\alpha V_0 c_0 \varepsilon_{\phi}^{\text{ini}} + V_{\text{KOH}} c_{\text{KOH}} (\varepsilon_{\phi}^{\text{fin}} - \varepsilon_{\phi}^{\text{ini}})} \quad (4)$$

Most parameters were fixed over the calculations (Φ_p , l , c_{KOH} , c_0 , V_0 , $\varepsilon_{\phi}^{\text{ini}}$ és $\varepsilon_{\phi}^{\text{fin}}$), the value of these were determined in independent experiments. The photon flux of the light source was determined based on actinometry. Reflection and scattering of the light were taken into account at the determination of the optical path length.

First, the product ratio of **QR-H₂**:**QR-OH** = 2:1 was used, as can be found in the literature [20]. However, the curves thus fitted were not in a good agreement with the measured kinetic curves. Therefore, a parameter α was introduced, which is the mole fraction of **QR-OH** in the photoproducts ($[\text{Q-OH}]/([\text{Q-OH}] + [\text{Q-H}_2])$). This parameter α was calculated upon fitting. Besides, the quantum yield of the photoreactions (Φ value) was calculated with equation (4), as it was the aim of the optimization of the technique.

I propose that the pH-stat technique with the created equation can be applied to study any photochemical reaction accompanied by pH change. Only the following parameters must be determined in independent experiments: the photon flux of the light source (1), the exact concentration of the acid or base used to set the pH constant (2), the optical light path (3), the initial concentration of the illuminated sample (4) and the initial sample volume (5). In addition, the value of the molar absorptivity must be measured in an independent experiment (6). Inert atmosphere, stirring of the sample and constant temperature must be provided throughout the measurement. After determining these 6 initial parameters and inserting them into the equation (4), the method can be applied to calculate the value of the quantum yield of the examined photochemical reaction simply and rapidly.

3. It was verified in independent experiments that the proposed pH-stat technique is well applicable to follow the photochemical reaction of different 1,4-benzoquinone derivatives.

It was necessary to verify the applicability of the proposed pH-stat technique with an independent measurement. Therefore, HPLC analyses were carried out to determine the concentrations of the formed photoproducts (**QR-OH** and **QR-H₂**) quantitatively and the concentration – time curves calculated in different ways were compared (Figure 3.).

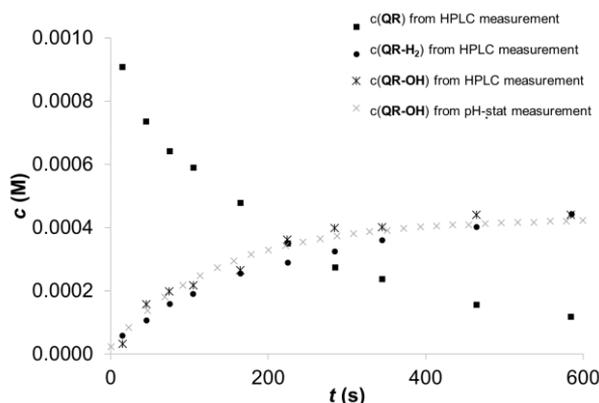


Figure 3: Determination of hydroxy-quinone concentration with HPLC és pH-stat techniques [11]

$$c(\mathbf{Q-2,5-Cl_2}) = 1.00 \cdot 10^{-3} \text{ M}, V(\mathbf{Q-2,5-Cl_2}) = 5.0 \cdot 10^{-2} \text{ dm}^3, \text{pH} = 3.97,$$

total illumination time = 10 min

The products were identified based on their UV spectra and elution order. The quinone solution (**Q-2,5-Cl₂**) was illuminated for 10 min, samples were taken periodically after different times and were analyzed by HPLC. The **QR-OH** concentrations obtained with the two different techniques were in good agreement (Figure 3).

4. It was proved that the kinetic curves recorded in the concentration-, temperature- and pH-dependent measurements of the QR-sulfur(IV) reactions can be fitted with double exponential functions even under non-pseudo-first order circumstances. A model for the QR-sulfur(IV) reaction was proposed.

Kinetic curves detected during the concentration-, temperature- and pH-dependent kinetic measurements were fitted at a single wavelength and then together at two different wavelengths with the double exponential function. Under the same experimental conditions, the same pseudo-first order rate constants were obtained by using the fittings with only one or two different wavelengths. Figure 4 shows an example of these fittings, with the dots representing the measurement data and the lines representing the fitted curves.

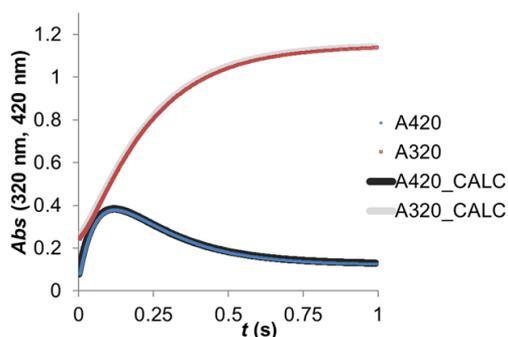
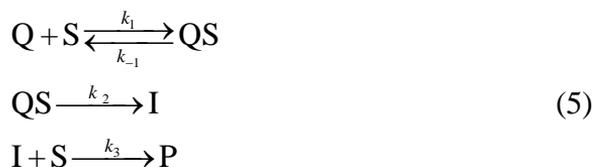


Figure 4: Fittings of the absorbance change in the reaction of **Q-2,5-Cl₂** and sulfur(IV) with double exponential function in the MicroMath Scientist software

$$c(\mathbf{Q-2,5-Cl}_2) = 0.50 \text{ mM}, c(\text{S(IV)}) = 1.00 \text{ mM}, t_{\text{total}} = 1 \text{ s},$$

$$(\text{acetate buffer}) \text{ pH} = 4.5, I = 1.0 \text{ M}, T = 298.2 \text{ K}$$

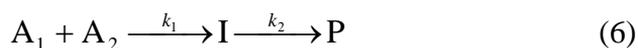
Exponential fitting is used widely. However, it is only trivial when one reactant is present in large excess. In my measurements, the concentrations of the reactants were comparable, but the obtained kinetic curves were still well characterizable by fitting the measured data with a double exponential function. A kinetic model was proposed for the reaction, as follows:



5. The mathematical description of the model reaction

$A_1 + A_2 \xrightarrow{k_1} I \xrightarrow{k_2} P$ proved that the scaled kinetic curves can be fitted with double exponential functions. It was also proved that the values of the pseudo-first order rate constants determined in the experiments can be estimated well prior to the global fitting.

To describe the QR-sulfur(IV) reaction, a model (5) was built. MicroMath Scientist and ZiTa softwares were used for the calculations. Along with the most concentration ratios, the reverse process of the first reaction step was negligible. Thus, it was not taken into account in the simplified model (6).



In the applied model, A_1 and A_2 represent two different reactants. In the first step of the reaction of these two reactants, several – non-reactive – products can be formed besides I, but they do not affect the mathematical description of the reaction.

Although the analytical solution for most two-step processes is known [21–23], the numerical solution of the differential equation system is simple, which can be given with fitting software.

There were 6 parameters in equation (6): 4 initial concentrations and 2 rate constants. In the analysis, it was suggested that no intermediate or product but only the 2 reactants (A_1 and A_2) were present initially. It was advantageous to use scaled concentrations (a_1 , a_2 , b , c), a scaled rate coefficient (κ), the ratio of A_1 and A_2 (σ) and scaled time for the calculations. With these scaled quantities, the differential equations contained only 2 parameters: κ and σ .

Kinetic curves were generated in the mathematical analysis to eliminate experimental error, which resulted in a 10×11 matrix. The parameter set was the following: $10 \geq \sigma \geq 1$ and $10 \geq \kappa \geq 0.1$. The generated curves were fitted with double exponential function (Figure 5).

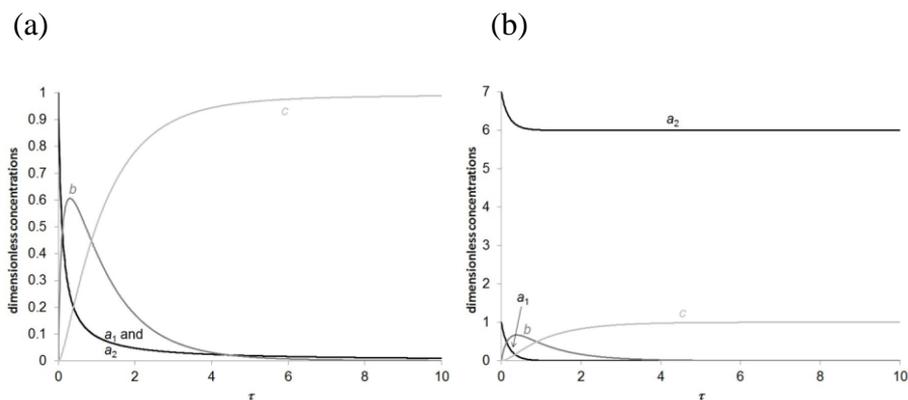


Figure 5: Simulated kinetic curves: change of the dimensionless concentrations of A_1 , A_2 , P and I (a_1 , a_2 , b , c) as a function of the scaled time (τ) [24]

(a): $\kappa = 10$, $\sigma = 1$, (b): $\kappa = 8$, $\sigma = 7$

The errors of the fittings and the values of the obtained pseudo-first order rate coefficients were examined. It was proved with comprehensive mathematical analysis that on the basis of model (6), the kinetic curves can be approximated well with double exponential functions. However, the exact description is only possible with complicated mathematical formulas (with hypergeometric function).

The pseudo-first order rate coefficients of the **QR**-sulfur(IV) reaction can be estimated well according to Figure 6, even before the global fitting, based on the pseudo-first order rate constants of the double exponential fitting of the absorbance-time curves measured at different concentration ratios (κ_1^m and κ_2^m).

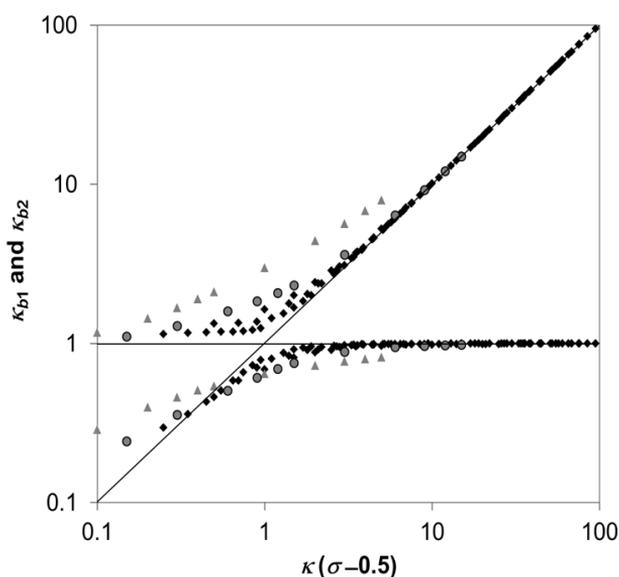


Figure 6: Scaled rate coefficient values (κ_{b1}, κ_{b2}) obtained from the double exponential fittings of the simulated kinetic curves as a function of $\kappa(\sigma - 0.5)$.

Both axis are logarithmic.

(Grey triangles and grey circles show values for $\sigma = 1$ and $\sigma = 2$, black markers show the results of every other calculations.) [24]

Possible utilization of the results

The proposed pH-stat technique is applicable for determining the quantum yield of other photochemical reactions if the reaction is accompanied by a pH change. Only the above-mentioned 6 parameters need to be determined in independent experiments that should be inserted into equation (4). The determination of the quantum yield is useful, it helps deciding if the given substance is potentially applicable for solar energy utilization or not.

The full quantitative description of reactions is an important aim in the field of chemistry. The exact interpretation of the measurement data obtained during the experimental observations or building a model is a central issue in chemical kinetics. Exponential fitting can be used generally. However, it is only based on observations in most of the kinetic research. With the studied simple model (6), it is now proved that the description of kinetic curves under non-pseudo-first order circumstances is possible with the application of double exponential function.

Publications

List of publications related to the dissertation

1. Virág Kiss, Gábor Lehoczki, Katalin Ósz
Mathematical description of pH-stat kinetic traces measured during photochemical quinone decomposition
Photochemical & Photobiological Sciences, **2017**, 16, 519-526.
IF: 2.344
2. Virág Kiss, Katalin Ósz
Double Exponential Evaluation under Non-Pseudo-First-Order Conditions: a Mixed Second Order Process Followed by a First Order Reaction
International Journal of Chemical Kinetics, **2017**, 49, 602-610.
IF: 1.416
3. Éva Józsa, Virág Kiss, Katalin Ósz
Photochemical Processes of 1,4-Benzoquinones in Aqueous Medium
Journal of Photochemistry and Photobiology A: Chemistry, **2018**, 360, 166-173.
IF: 2.891 (2017)

List of other publications

4. Éva Józsa, Mihály Purgel, Marianna Bihari, Péter Pál Fehér, Gábor Sustyák, Balázs Várnagy, Virág Kiss, Eszter Ladó, Katalin Ósz
Kinetic studies of hydroxyquinone formation from water soluble benzoquinones
New Journal of Chemistry, **2014**, 38, 588-597.
IF: 3.086



Registry number: DEENK/285/2018.PL
Subject: PhD Publikációs Lista

Candidate: Virág Kiss
Neptun ID: X7YCSA
Doctoral School: Doctoral School of Chemistry
MTMT ID: 10051332

List of publications related to the dissertation

Foreign language scientific articles in international journals (3)

1. Józsa, É., **Kiss, V.**, Ósz, K.: Photochemical processes of 1,4-benzoquinones in aqueous medium.
J. Photochem. Photobiol. A-Chem. 360, 166-173, 2018. ISSN: 1010-6030.
DOI: <http://dx.doi.org/10.1016/j.jphotochem.2018.04.024>
IF: 2.891 (2017)
2. **Kiss, V.**, Ósz, K.: Double Exponential Evaluation under Non-Pseudo-First-Order Conditions: A Mixed Second-Order Process Followed by a First-Order Reaction.
Int. J. Chem. Kinet. 49 (8), 602-610, 2017. ISSN: 0538-8066.
DOI: <http://dx.doi.org/10.1002/kin.21100>
IF: 1.416
3. **Kiss, V.**, Lehoczki, G., Ósz, K.: Mathematical description of pH-stat kinetic traces measured during photochemical quinone decomposition.
Photochem. Photobiol. Sci. 16 (4), 519-526, 2016. ISSN: 1474-905X.
DOI: <http://dx.doi.org/10.1039/C6PP00333H>
IF: 2.344





List of other publications

Foreign language scientific articles in international journals (1)

4. Józsa, É., Purgel, M., Bihari, M., Fehér, P. P., Sustyák, G., Várnagy, B., **Kiss, V.**, Ladó, E., Ósz, K.: Kinetic studies of hydroxyquinone formation from water soluble benzoquinones.
New J. Chem. 38 (2), 588-597, 2014. ISSN: 1144-0546.
DOI: <http://dx.doi.org/10.1039/c3nj01274c>
IF: 3.086

Total IF of journals (all publications): 9,737

Total IF of journals (publications related to the dissertation): 6,651

The Candidate's publication data submitted to the iDEa Tudóstér have been validated by DEENK on the basis of Web of Science, Scopus and Journal Citation Report (Impact Factor) databases.

24 August, 2018



Hivatkozások/References

- [1] R.A. Berner, The long-term carbon cycle, fossil fuels and atmospheric composition, *Nature*. 426 (2003) 323–326.
- [2] M. Hook, X. Tang, Depletion of fossil fuels and anthropogenic climate change, *Energy Policy*. 52 (2012) 797–809.
- [3] S.K. Michael Hoel, Depletion of fossil fuels and the impacts of global warming, *Resour. Energy Econ.* 18 (1996) 115–136.
- [4] M.S. Dresselhaus, I.L. Thomas, Alternative energy technologies, *Nature*. 414 (2001) 332–337.
- [5] J.S. Machele, S.S. Haramkar, V.C. Renge, Review on solar fuels, *Sci. Rev. Chem. Commun.* 3 (2013) 100–109.
- [6] Y. Tian, C.Y. Zhao, A review of solar collectors and thermal energy storage in solar thermal applications, *Appl. Energy*. 104 (2013) 538–553.
- [7] T.J. Monks, R.P. Hanzlik, G.M. Cohen, D. Ross, D.G. Graham, Quinone chemistry and toxicity, *Toxicol. Appl. Pharmacol.* 112 (1992) 2–16.
- [8] S.E. Hrudey, J.W.A. Charrois, *Disinfection by-products : relevance to human health*, IWA, London, 2012.
- [9] C.M. Villanueva, K.P. Cantor, J.O. Grimalt, N. Malats, D. Silverman, A. Tardon, R. Garcia-Closas, C. Serra, A. Carrato, G. Castano-Vinyals, R. Marcos, N. Rothman, F.X. Real, M. Dosemeci, M. Kogevinas, Bladder cancer and exposure to water disinfection by-products through ingestion, bathing, showering, and swimming in pools, *Am. J. Epidemiol.* 165 (2006) 148–156.
- [10] A. Jemal, F. Bray, M.M. Center, J. Ferlay, E. Ward, D. Forman, Global cancer statistics, *CA. Cancer J. Clin.* 61 (2011) 69–90.
- [11] V. Kiss, G. Lehoczki, K. Osz, Mathematical description of pH-stat kinetic traces measured during photochemical quinone decomposition, *Photochem. Photobiol. Sci.* 16 (2017) 519–526.
- [12] B. Tonomura, H. Nakatani, M. Ohnishi, J. Yamaguchi-Ito, K. Hiromi, Test reactions for a stopped-flow apparatus: reduction of

- 2,6-dichlorophenolindophenol and potassium ferricyanide by l-ascorbic acid, *Anal. Biochem.* 84 (1978) 370–383.
- [13] U. Salt Lake City, Scientist 2.01, MicroMath Software, (1995).
- [14] G. Peintler, ZiTa, version 5.0; a comprehensive program package for fitting parameters of chemical reaction mechanism, University, Szeged, Hungary, (n.d.).
- [15] I. The Mathworks, MatLab for Windows, version 4.2c1, Natick, MA, USA, (1994).
- [16] F. Poupe, A polarographic investigation of photochemical changes in quinones, *Collect. Czechoslov. Chem. Commun.* 12 (1947) 225–236.
- [17] H.-I. Joschek, S.I. Miller, Photooxidation of phenol, cresols, and dihydroxybenzenes 1,2, *J. Am. Chem. Soc.* 88 (1966) 3273–3281.
- [18] K.C. Kurien, P.A. Robins, Photolysis of aqueous solutions of p-benzoquinone: a spectrophotometric investigation, *J. Chem. Soc. B.* (1970) 855–859.
- [19] É. Józsa, V. Kiss, K. Ósz, Photochemical processes of 1,4-benzoquinones in aqueous medium, *J. Photochem. Photobiol. A Chem.* 360 (2018) 166–173.
- [20] G. Lente, J.H. Espenson, Photoreduction of 2,6-dichloroquinone in aqueous solution: Use of a diode array spectrophotometer concurrently to drive and detect a photochemical reaction, *J. Photochem. Photobiol. A Chem.* 163 (2004) 249–258.
- [21] G. Lente, *Deterministic kinetics in chemistry and systems biology*, 1st ed., Springer International Publishing, Cham Heidelberg New York Dordrecht London, 2015.
- [22] J.H. Espenson, *Chemical kinetics and reaction mechanisms*, 2nd Editio, McGraw-Hill, New York, 1995.
- [23] P. Érdi, G. Lente, *Stochastic Chemical Kinetics. Theory and (Mostly) Systems Biological Applications*, Springer-Verlag, Heidelberg, New York, Dordrecht, London, 2014.
- [24] V. Kiss, K. Osz, Double exponential evaluation under non-pseudo-first-order conditions: A mixed second-order process followed by a first-order reaction, *Int. J. Chem. Kinet.* 49 (2017) 602–610.