Analytisch-Physikalische Chemie

Teil Physikalische Chemie
Sommersemester 2007

Determination velocity-constant of 1',3',3'-Trimethyl-6-hydroxyspiro(2H-1-benzylpyran)-2,2'-indoline in different solvent and at different temperature.
(BLP)

Matthias Geibel, *Studiengang Chemie, 4. Semester*, mgeibel@student.ethz.ch
Daniel A. Frick, *Studiengang Chemie, 4. Semester*, frickd@student.ethz.ch

Assistant: Edouard Miloglyadov

Abstract: In the following experiment the velocity-constant of 1',3',3'-Trimethyl-6-hydroxyspiro(2H-1-benzylpyran)-2,2'-indoline in five different solvents and at different temperature in cyclohexane was determined using the photo-flash-method. For the following solvent the velocity-constant were determined, 2-Propanol (0,0235 ± 0,0017 s^{-1}), Ethanol (0,579 ± 0,020 s^{-1}), 1,4-Dioxane (4,60 ± 0,17 s^{-1}), Cyclohexane (10,1 ± 1,8 s^{-1}) and Methylcyclohexane (12,82 ± 0,21 s^{-1}). For the following temperature the velocity-constant at the temperature of 20 °C (7,4 ± 0,3 s^{-1}), 30 °C (16,16 ± 0,25 s^{-1}), 40 °C (25,22 ± 0,03 s^{-1}), 45 °C (31,3 ± 0,9 s^{-1}), 50 °C (33,3 ± 1,2 s^{-1}) and 60 °C (47,3 ± 2,2 s^{-1}) were determined.

From the Arrhenius equation the activation energy was calculated, the value for the used photo chrome is: 801 ± 52 J/mol.

Zürich ZH, 11. April 2007

Matthias Geibel

Daniel A. Frick

1. Introduction

1.1. Theory

Photo chrome

Substances, which change their colour under certain light and change back to the original colour again when removing the light are called photo chrome. The common, reversible photo chrome process can be described by:

$$R(\lambda_R)\overset{k_{RP},h\upsilon_R}{\xleftrightarrow{-k_{PR},h\upsilon_P}}P(\lambda_P)\ \textbf{(1)}$$

The reactant R, which is characterized by the absorbance maximum λ_R, changes under a certain frequency and energy, with the constant k_{RP}, into the product P, which is characterized by the absorbance maximum at a different λ_P. The reaction in the other direction has its own reaction constant k_{PR} and energy which is needed to get back to the thermodynamically more stable reactant R.

Determination of the change in absorbance

The best quantity to measure the determination of the velocity of the reaction is the difference between the absorbance before, after the illumination with a flash and during the relaxation. The absorbance of a sample can be described as:

$$A_\lambda^{eq}=d\sum_i \varepsilon_{\lambda,i}c_i^{eq}=-\log_{10}T_\lambda^{eq}=\log_{10}\frac{U_\lambda^{0}}{U_\lambda^{eq}}\ \textbf{(2)}$$

Were A_λ^{eq} is the absorbance at the equilibrium, T_λ^{eq} the transmission of the sample. Before using the flash the absorbance of the sample is constant. When now using the flash, the absorbance has now to be measured as a function of time:

$$A_\lambda(t)=d\sum_i \varepsilon_{\lambda,i}c_i(t)=-\log_{10}T_\lambda(t)=\log_{10}\frac{U_\lambda^{0}}{U_\lambda(t)}\ \textbf{(3)}$$

The change in absorbance can be calculated as:

$$\Delta A_\lambda(t)=A_\lambda(t)-A_\lambda^{eq}\ \textbf{(4)}$$

The change in absorbance can be expressed by using the concentration of the particle:

$$\Delta A_\lambda(t)=d\left[\sum_i \varepsilon_{\lambda,i}c_i(t)-\sum_i \varepsilon_{\lambda,i}c_i^{eq}\right]\ \textbf{(5)}$$

And there for the change in concentration can be expressed as:

$$\Delta c_i(t)=c_i(t)-c_i^{eq}\ \textbf{(6)}$$

Spectrochemical measurement of the reaction velocity

The reaction velocity at a homogenous reaction

$$\sum_i B_i v_i=0\ \textbf{(7)}$$

is defined as:

$$v_c(t)=\frac{1}{v_i}\frac{dc_i(t)}{dt}=\frac{1}{v_i}\frac{\Delta c_i(t)}{dt}\ \textbf{(8)}$$

Using equation 5 and 6 the velocity of the reaction can be described as

$$v_c(t)=\frac{1}{d\sum_i v_i\varepsilon_{\lambda,i}}\frac{dA_\lambda(t)}{dt}\ \textbf{(9)}$$

First order kinetic

For the reaction P → R and the concentration $c_P(t)$ and $c_R(t)$ which change in respect of time, the velocity of the reaction is:

$$v_c(t) = \frac{dc_P(t)}{dt} = \frac{dc_R(t)}{dt} \quad \textbf{(10)}$$

The ansatz for the first order kinetic is

$$v_c(t) = k \cdot c_p(t) \quad \textbf{(11)}$$

and where k is the reaction-velocity-constant. Using equation 11 in eqution 9, rearrange and then enter it in equation 10 and expressing it in the change of absorbance is:

$$-k\Delta A_\lambda(t) = \frac{d\Delta A_\lambda(t)}{dt} \quad \textbf{(12)}$$

Separation and integration, using $\Delta A_\lambda(t = 0) = \Delta A_\lambda(0)$:

$$\Delta A_\lambda(t) = \Delta A_\lambda(0) \cdot \exp(-kt) \quad \textbf{(13)}$$

The reaction-velocity-constant can be obtained by a linear regression application of $\ln[\Delta A_\lambda(t)]$ vs. $\frac{1}{T}$.

Temperature dependence of the reaction-velocity-constant

Out of the temperature dependence of the reaction-velocity-constant under the help of the differential Arrhenius-relation, the Arrhenius-activation-energy $E_A(T)$ can be calculated:

$$\frac{d \ln k(T)}{d(1/T)} = -\frac{E_A(T)}{R} \quad \textbf{(14)}$$

At a certain bounded area of the temperature, the activation energy $E_A(T)$ is constant, the integration of equation (14) delivers:

$$k(T) = A \cdot \exp\left(-\frac{EA}{RT}\right) \quad \textbf{(15)}$$

2. Experiment

2.1. Experimental setup

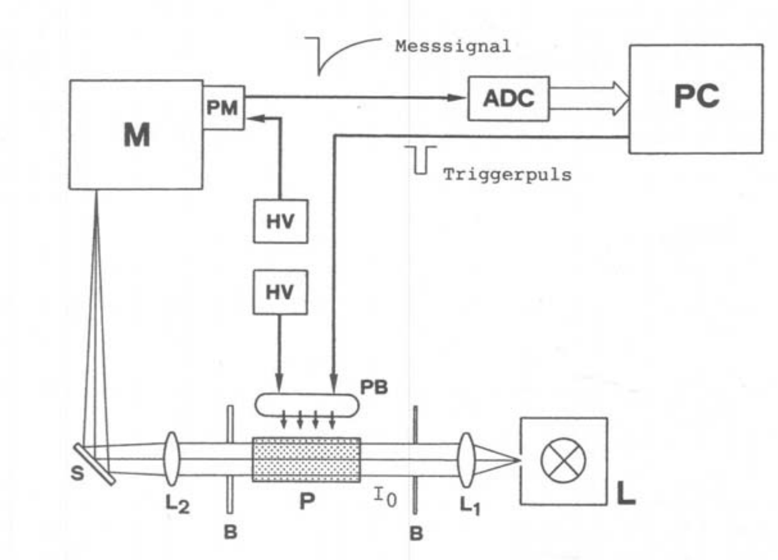

Abb. 1: Schematically picture of the experimental setup. ADC is the analog digital converter, B is the aperture, F is a color-filter, HV is the highvoltage-supplyunit, IB the iris-aperture, L the halogen lamp, L1 and L2 the lenses, M the grind-monochromator, P the sample in a thermostatic cell, PB the photo-flash, PC the personal computer, PM the photo multiplier and S a mirror.[1]

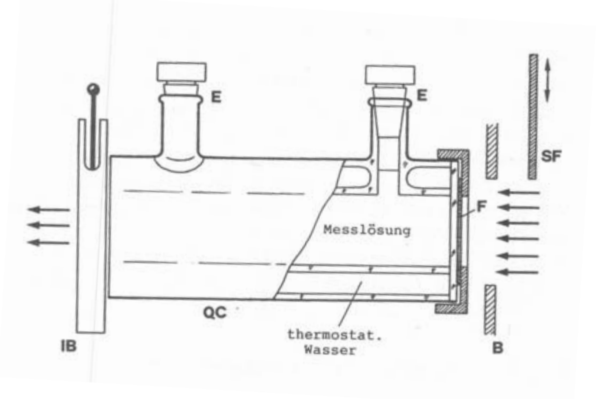

Abb. 2: Schematically picture of the sample cell. QC is the thermostatic quartz-cell, E the filling tube for the cell, F the color filter, IB the iris-aperture and SF the movable steal-foil. [1]

The used setup is presented in Abb. 1 and Abb. 2. Photo-flash-spectrometer is a modified Applied Photophysics Model 858. The Xenon-flashlamp has a maximum energy of about 40 J, the FWHM (puls-width) is about 50µs. A Wolfram-halogen lamp (L) produces the light for the polychromatic observation-beam. The beam passes through the sample-cell, which is tempered by LAUDA MT3, the signal goes through a grid-monochromator, which selects the chosen wavelength and passes it on to a photomultiplier, which multiplies the signal coming from the monochromator. From the photomultiplier the signal is passed through an analog digital converter and measured and saved on a personal computer. The kinetic measurement consists of 1000 measured points of $U_\lambda(t_i)$ and the intensity of the light $I_\lambda(t)$. The points were taken in constant time-distance.

2.2. Substances

1',3',3'-Trimethyl-6-hydroxyspiro(2H-1-benzylpyran)-2,2'-indoline	M:	293.36 g/mol
	Hazard:	XN
	Risk:	20/21/22 36/37/38
	Safety:	24/25 26 37/39
Cyclohexane	M:	84.16 g/mol
	Hazard:	F XN N
	Risk:	11 38 50/53 65 67
	Safety:	9 16 33 60 61 62
	bp (°C):	80- 82
	mp (°C):	6.5
	density:	0.77 kg/l
Methal-cyclohexane	M:	98.19 g/mol
	Hazard:	F XN N
	Risk:	11 38 51/53 65 67
	Safety:	9 16 33 61 62
	bp (°C):	101
	density:	0.77 kg/l
Ethanol	M:	46.07 g/mol
	Hazard:	F
	Risk:	11
	Safety:	7 16 9 33
	bp (°C):	78
	density:	0.78 kg/l
2-Propanol	M:	60.10 g/mol
	Hazard:	F XI
	Risk:	11 36 67
	Safety:	7 16 24/25 26
	bp (°C):	81
	mp (°C):	-90 - -88
	density:	0.78 kg/l
1,4-Dioxane	M:	88.11 g/mol
	Hazard:	F XN
	Risk:	11 19 36/37 40 66
	Safety:	9 16 36/37 46 66
	bp (°C):	101
	mp (°C):	12
	density:	1.03 kg/l

Tab. 1: Chemical information of the Substance which were used during the experiment [2]

2.3. Execution of the experiment

For the change of sample, the sample cell was washed several times with the solvent and then filled up with the solutions which were prepared by using a scale from Mettler Toledo and a 50ml-volumetric-flask. Every measurement was made at least three times with the same settings.

2.3.1. Optimization

To find out the best parameters to use with the substance some pre-experiments ware made. The first was to measure the pm-amplification, so that there isn’t any overshoot. The second was to determine the voltage of the flash, so that the whole substance reacts. The last one was to determine the optimum wave length, where the reaction could be observed best.

2.3.2. The solvent dependence

From every solvent (Ethanol, Cyclohexane, Methyl-cyclohexane, 2-Propanol and 1,4-Dioxane) a 1 mmol solution of 1’,3’,3’-Trimethyl-6-hydroxyspiro(2H-1-benzylpyran)-2,2’-indoline was prepared, the cell was cleaned as described above and filled up. A first test with every solvent was made to determine the duration of the experiment, the offset and the resolution of the voltage. Then the sample was measured three times at the same temperature (30 °C)

2.3.3. The temperature dependence

The best solvent (Cyclohexane) from the solvent dependence experiment was taken (0.2 mmol solution) and temperature was varied (20 °C, 30 °C, 40 °C, 45 °C, 50 °C and 60°C). The relaxation-time was measured but the PM voltage, the flash voltage and the voltage resolution weren’t changed during the experiment.

2.3.4. The wave-length dependence

The same solvent from the previous experiment was tempered at 30°C, the PM voltage, the flash-voltage and the resolution of the voltage weren’t changed during the experiment. Only the wavelength was varied (300nm, 400nm, 500nm, 600nm, 700nm, 800nm) and the relaxation-time was measured.

3. Analysis and Results

3.1. Mechanism of the used photo chrome

As the photo chrome 1',3',3'-Trimethyl-6-hydroxyspiro-(2H-1-benzopyran)-2,2'-indoline was used. After irradiation with UV light the C-O bond opens, resulting a planar and conjugated system. This system absorbs light of visible radiation.

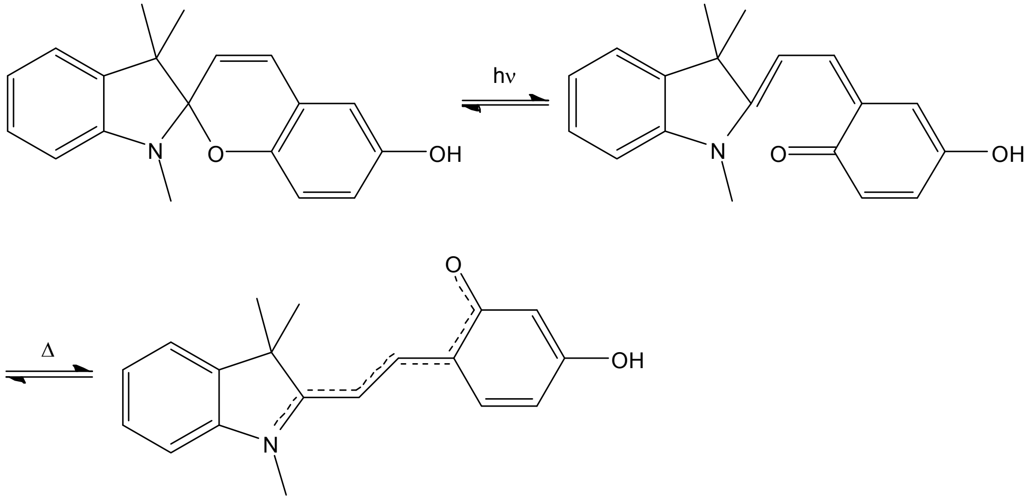

Abb. 3: Photochromism of 1',3',3'-Trimethyl-6-hydroxyspiro-(2H-1-benzopyran)-2,2'-indoline.

3.2. Dependence of velocity of reverse reaction on solvents

Solvent	k_{eff} / s^{-1}
2-Propanol	0,0235 ± 0,0017
Ethanol	0,579 ± 0,020
1,4-Dioxane	4,60 ± 0,17
Cyclohexane	10,1 ± 1,8
Methylcyclohexane	12,82 ± 0,21

Tab. 2: Dependence of velocity of reverse reaction on solvents.

3.3. Dependence of velocity of reverse reaction on temperature

Temperature / °C	k_{eff} / s^{-1}
20	7,4 ± 0,3
30	16,16 ± 0,25
40	25,22 ± 0,03
45	31,3 ± 0,9
50	33,3 ± 1,2
60	47,3 ± 2,2

Tab. 3: Dependence of velocity of reverse reaction on temperature in cyclohexane.

3.4. Determination of activation energy

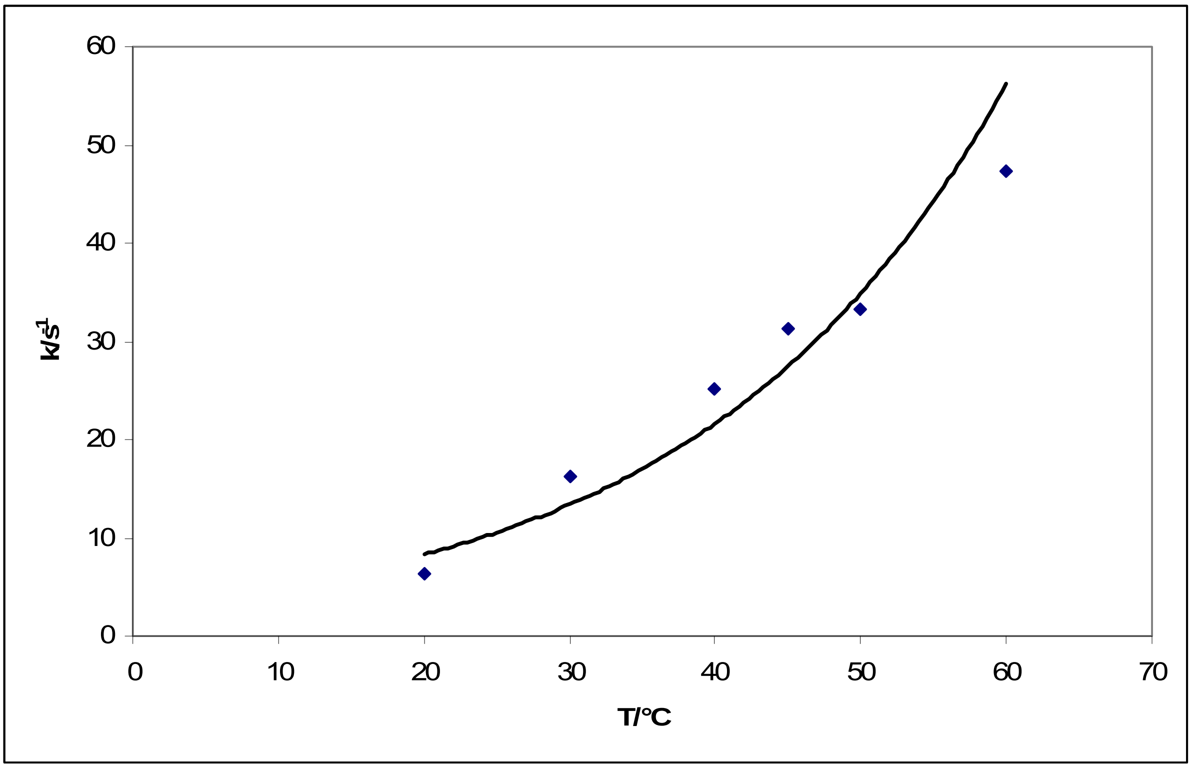

Abb. 4: Unlinearized data: k_{eff} plotted against Temperature.

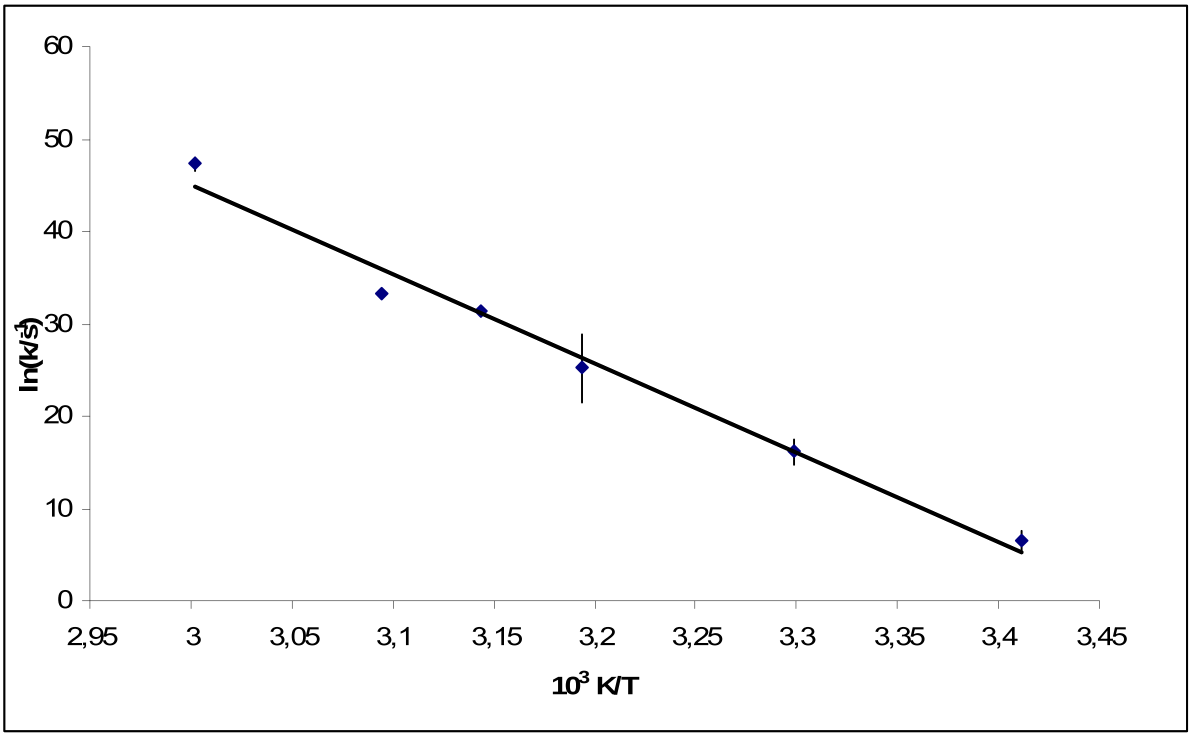

Abb. 5: Arrhenius linearisation of measured data.

The linear regression of the Arrhenius linearization gives:

y = (-96,308 ± 7) + (334 ± 22)

Using equation (14) one obtains for E_A:

E_A= 801 ± 52 J/mol

3.5. Dependence of absorbance on wavelength

The absorbance in cyclohexane was observed at different wavelength. There was an absorbance between 400 and 700 nm. The maximum absorbance was at 600 nm, what correspond to the literature. [3]

4. Discussion

Dependence on solvents

The experiment shows that the speed of the reverse reaction is connected to the solvent. In non-polar solvents is the reaction slower than in polar solvents (see Tab. 2). This can be explained with the stability of the reactant and the molecule after irradiation. The molecule after irradiation is more stable in non-polar solvents.
The speed of the reverse reaction was measured at 500 nm. Although this is not the optimal wavelength there were no problems.

Activation energy

The activation energy was determined at a wavelength of 600 nm. The calculated value for the activation energy is 801 ± 58 J/mol. A reference value was not found. In order to obtain a better value with reference to the error, it is necessary to increase the number of measurements.

Dependence of absorbance on wavelength

During the determination of the best wavelength it was observed, that the speed of the reaction also changes with the wavelength.

5. Appendix

5.1. Experimental raw data

5.1.1. Dependence of velocity of reverse reaction on solvents

Run	k_{eff} / s^{-1}	Average / s^{-1}	STDEV / s^{-1}	Confidence of interval (95 %) / s^{-1}
1	0,0240128	0,02354947	0,00070577	0,001752137
2	0,0238984			
3	0,0227372			

Tab. A1: Noted down values for velocity of reverse reaction in 2-Propanol

Run	keff / s-1	Average / s-1	STDEV / s-1	Confidence of interval (95 %) / s^{-1}
1	9,3201	10,1321	0,71142733	1,76619386
2	10,6459			
3	10,4303			

Tab. A2: Noted down values for velocity of reverse reaction in Cyclohexane.

Run	k_{eff} / s^{-1}	Average / s^{-1}	STDEV / s^{-1}	Confidence of interval (95 %) / s^{-1}
1	9,3201	12,8242	0,082659	0,205209738
2	10,6459			
3	10,4303			

Tab. A3: Noted down values for velocity of reverse reaction in Methylcyclohexane

Run	k_{eff} / s^{-1}	Average / s^{-1}	STDEV / s^{-1}	Confidence of interval (95 %) / s^{-1}
1	4,59395	4,56732833	0,09701185	0,240842214
2	4,64825			
3	4,459785			

Tab. A4: Noted down values for velocity of reverse reaction in 1,4-Dioxane.

Run	k_{eff} / s^{-1}	Average / s^{-1}	STDEV / s^{-1}	Confidence of interval (95 %) / s^{-1}
1	0,576741	0,579194	0,00811065	0,020135553
2	0,572593			
3	0,588248			

Tab. A5: Noted down values for velocity of reverse reaction in Ethanol.

5.1.2. Dependence of velocity of reverse reaction on temperature

Run	Temperature / °C	k_{eff} / s^{-1}	Average / s^{-1}	STDEV / s^{-1}	Confidence of interval (95 %) / s^{-1}
1	20	7,30255	7,42733333	0,13868085	0,344289926
2	20	7,57664			
3	20	7,40281			
1	30	16,145	16,1567333	0,09892327	0,245587519
2	30	16,261			
3	30	16,0642			
1	40	25,2059	25,2165	0,0103131	0,025603362
2	40	25,2265			
3	40	25,2171			
1	45	31,7419	31,3402	0,35103628	0,871484831
2	45	31,1863			
3	45	31,0924			
1	50	33,0618	33,3367333	0,49774257	1,235698763
2	50	33,0371			
3	50	33,9113			
1	60	46,3163	47,2986667	0,89081896	2,211552641
2	60	47,5257			
3	60	48,054			

Tab. A6: Determination of k_{eff} in Cyclohexane in dependence on temperature.

5.2. Error calculation for the Arrhenius linearization

The linear regression was carried out with Microsoft Exel:

Regressions-Statistik	
Multipler Korrelationskoeffizient	0,988538704
Bestimmtheitsmaß	0,97720877
Adjustiertes Bestimmtheitsmaß	0,969611693
Standardfehler	1,99606549
Beobachtungen	5

	Freiheitsgrade (df)	***Quadratsummen (SS)***	***Mittlere Quadratsumme (MS)***	***Prüfgröße (F)***	***F krit***
Regression	1	999,1796442	999,1796442	266,174127	8,2608E-05
Residuen	4	15,01542849	3,753857122		
Gesamt	5	1014,195073			

	Koeffizienten	***Standardfehler***	***t-Statistik***	***P-Wert***	***Untere 95%***	***Obere 95%***
Schnittpunkt	334,1506641	18,86576112	17,71201606	5,96906E-05	281,770914	386,530414
X Variable 1	-96,38837617	5,908017109	-16,31484378	8,26075E-05	-112,791661	-79,985091

Beobachtung	***Schätzung für Y***	***Residuen***	***Standardisierte Residuen***
1	5,348425716	1,078907617	0,622587499
2	16,19461534	-0,037882003	-0,021859946
3	26,34808967	-1,13158967	-0,652987866
4	31,18547101	0,154728995	0,08928692
5	35,87315773	-2,536424397	-1,46365277
6	44,82640721	2,472259459	1,426626163

5.2.1. Calculation for E_A

E_A= -R·m= 801.421 J mol^{-1}
Standard deviation of slope m: 5.90801
Standard deviation: $s(E_A) = R \cdot s(m)$ = 49.12206 J mol^{-1}
Interval of confidence: $\pm t_s \cdot s(E_A) / \sqrt{n}$ = 51.838 J mol^{-1}
(t_s = 2.57, n=6)

5.3. Dependence of absorbance on wavelength

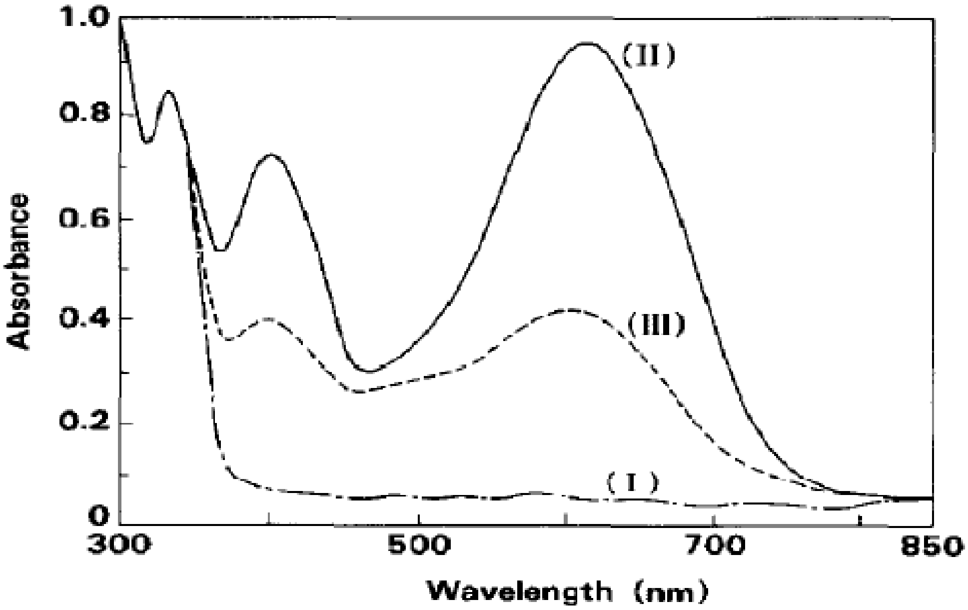

Abb. 5: UV-Visible spectra of 1',3',3'-Trimethyl-6-hydroxyspiro-(2H-1-benzopyran)-2,2'-indoline
(I) before UV and visible irradiation
(II) UV irradiated
(III) visible irradiated [3]

5.4. Raw Data

If wished, they can be downloaded at http://www.crew.li/blp

5.5. Literature

[1] E. Meister, Grundpraktiukum Physikalische Chemie; vdf Hochschulverlag AG; 2006
[2] http://www.chemexper.com, 07.04.2007.
[3] Takashi Yoshida,Akira Morinaka, and Nobuhiro Funakoshi; *J. CHEM. SOC., CHEM. COMMUN.*, **1986,** 437