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### Time Dependent UV-Vis Spectrum: A Simple Under-Graduate Physical Chemistry Experiment

**The meaning of the time dependent UV-Vis spectrum and its recording in the physical chemistry laboratory are explained. The hydrolysis of benzal chloride (=  $\alpha,\alpha$ -dichlorotoluene=(dichloromethyl) benzene) is used as an example.**

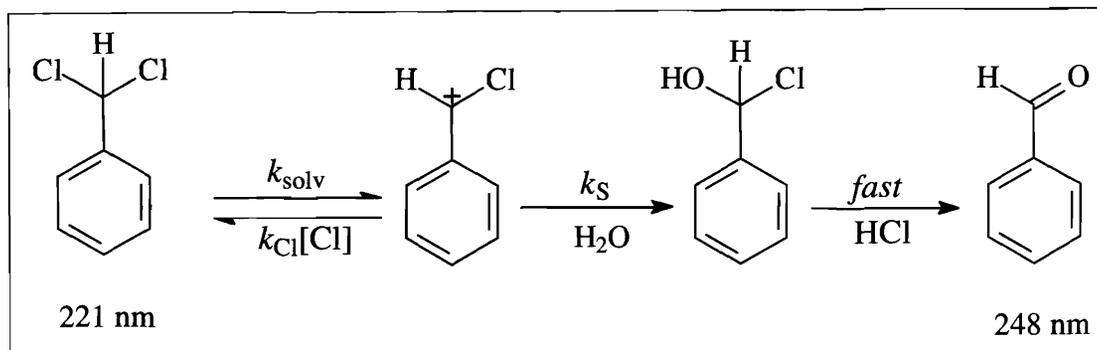
If change in the concentration of the reactant or the product in a reaction can be measured, it is possible to determine the rate constant for that reaction. The method used to monitor the concentrations depends on the species involved and the rapidity with which their concentrations change. Reactions go to completion or reach equilibrium in seconds to hours or even days to years. Several techniques are used to follow the changing concentrations. For a reaction in which one of the components is a gas, its progress may be followed by recording the variation of its pressure with time at constant volume. Solution phase reactions can be followed by titration. If the number or type of ions present in solution change during the course of the reaction, it can be followed by monitoring the conductivity of the solution. If hydrogen ions are produced or consumed during the reaction, then it can be followed by monitoring the pH of the solution. Several other methods include mass spectrometry, gas chromatography, magnetic resonance, high performance liquid chromatography, polarimetry, infrared, Raman and UV-Vis spectroscopy.

A simple and effective method of monitoring a reaction is spectrophotometry. The measurement of the intensity of absorption in a particular spectral region is widely applicable and is especially useful when one substance (and only one) in the reaction mixture has a strong characteristic absorption in a conveniently accessible region of the spectrum.

#### Keywords

Solvolysis, hydrolysis, UV-Vis spectrum, kinetics.

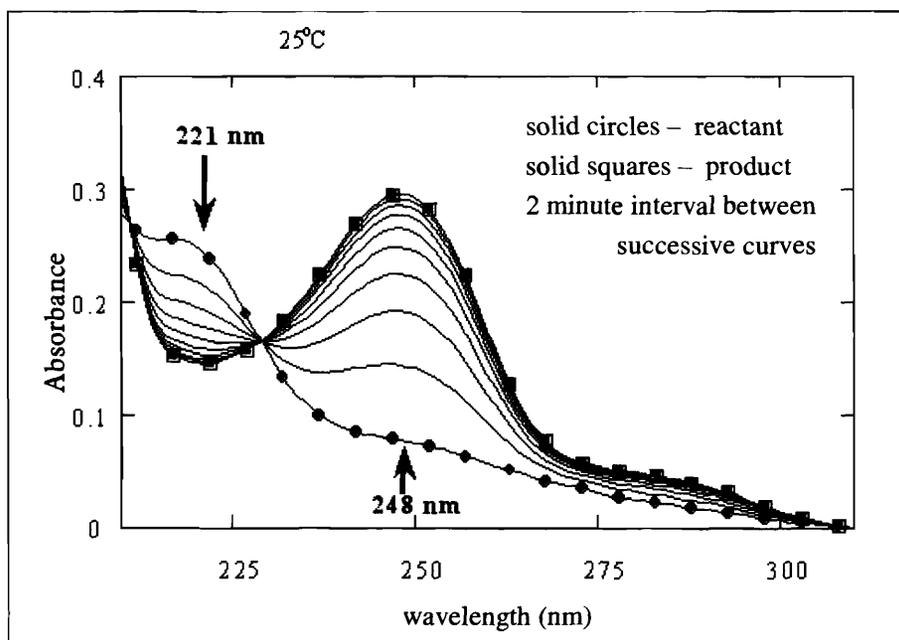
For a reaction which takes place in less than an hour (longer durations will damage the UV lamp) one can use a spectrophotometer to study its progress. Using a kinetics program in the



Scheme 1.

spectrophotometer one can follow the reaction by observing the change in absorbance with time at  $\lambda_{\text{max}}$  of either the reactant or the product. For this purpose one should have a knowledge of the absorption spectrum of the reactant and the product. This can be achieved by running the time dependent absorption spectrum of the reaction mixture. As an example, the time dependent absorption spectrum of benzal chloride ( $\text{C}_6\text{H}_5\text{CHCl}_2$ ) in water during solvolysis is shown in *Figure 1*. From the first run it is evident that the  $\lambda_{\text{max}}$  of the reactant ( $\text{C}_6\text{H}_5\text{CHCl}_2$ ) is 221 nm and from the last run  $\lambda_{\text{max}}$  of the product, benzaldehyde, is 248 nm. This is obtained by initiating the reaction of 30  $\mu\text{L}$  of 0.01

*Figure 1. Time dependent UV-Vis spectrum of benzal chloride in water at 25°C.*



molar solution of the substrate in acetonitrile in 3 mL of water in a spectrophotometric quartz cuvette of 3 mL capacity and 1 cm path length, and scanning the wavelength range several times. Here, ten scans of spectra were recorded on a UVIKON 923 model UV-Vis spectrophotometer at 2 minutes interval between successive scans. Obviously, the first scan is that of the reactant and the last one is that of the product. The intermediate scans demonstrate the changes in absorption with time of the reactant and the product. The essential condition for recording the time dependent absorption spectrum is that the difference between  $\lambda_{\max}$  of the product and the reactant must be at least 25 to 30 nm. Otherwise the spectrum obtained will be unclear. Further, it will be an added advantage if the ratio of the molar extinction coefficients of the product and the reactant is  $> 3$ . The spectrophotometer used need not necessarily be the one mentioned here. Any other spectrophotometer having simple automatic recording facility can be used.

Once the  $\lambda_{\max}$  of the reactant and the product are known, the kinetics can be followed at either of the  $\lambda_{\max}$ . *Figure 2* shows such kinetics curves for benzal chloride-benzaldehyde system. Using KaleidaGraph program (Synergy Software, USA) the rate constants can be calculated choosing a suitable program. Here it was a first order reaction; hence first order fit program was used.

A first order reaction is one which obeys the following differential rate law:

$$\frac{d[A]}{dt} = -k[A]; \quad \frac{d[P]}{dt} = k[P]$$

The equations indicate that the concentration of the reactant A (benzal chloride) decreases and the concentration of the product P (benzaldehyde) increases with time. To obtain the concentration of either the reactant or the product at different time intervals the equation has to be integrated between the limits at  $t=0$  when  $[A]=[A]_0$  and  $t=t$  when  $[A] = [A]$ . Hence,  $[A] = [A]_0 \exp(-kt)$ .

Using the experimental data obtained from the UV-Vis instrument and the following two equations provided in the KaleidaGraph



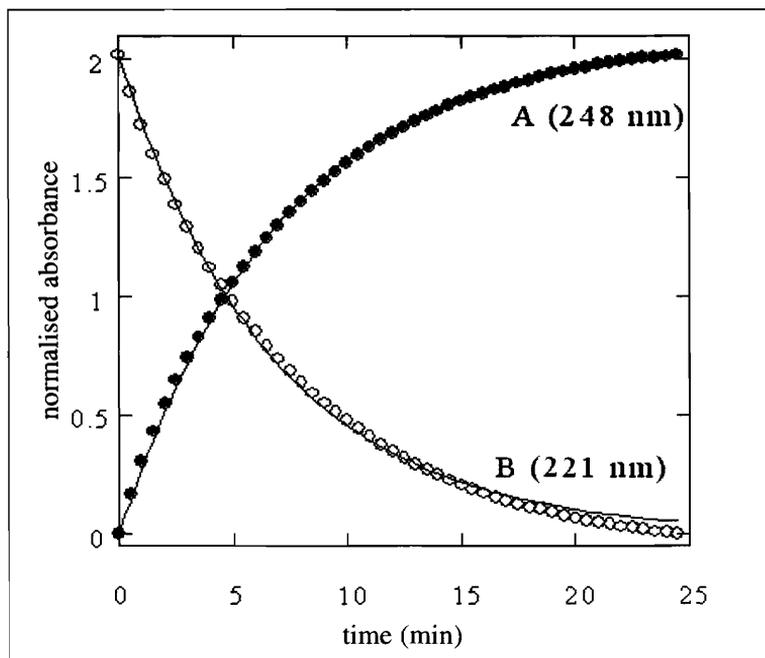


Figure 2. Curve A: Formation of benzaldehyde at 248 nm; Curve B: Decay of benzal chloride at 221 nm.

software, the rate constant  $k$  can be calculated.

$$y = m_1(1 - \exp(-m_2 \cdot m_0)) \quad \text{for formation of the product}$$

$$y = m_1(\exp(-m_2 \cdot m_0)) \quad \text{for depletion of the reactant}$$

The '\*' indicates multiplication.

Here 'y' is the concentration of either the reactant or the product at a given point of time, i.e. [A] or [P], and 'm1' is the concentration at infinite time, 'm2' is the rate constant 'k' and 'm0' is the time. While solving these equations using the KaleidaGraph program some arbitrary values of 'm1' and 'm2' have to be given to the program so that after a number of iterations the software gives the rate constant and the correlation coefficient. The value of the rate constant 'k' calculated this way was found to be  $2.37 \times 10^{-3} \text{ sec}^{-1}$  for the formation of the product and  $2.48 \times 10^{-3} \text{ sec}^{-1}$  for the depletion of the reactant which are in good agreement with each other within experimental error. The correlation coefficient is 0.999 for both the processes. It is not necessary to use only the KaleidaGraph program for this work. Any other program such as 'Microcal origin' can also be used.

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