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KİMYASAL KİNETİKTE DİFERANSİYEL SPEKTROFOTOMETRİ : METİL SALİSİLATIN YALANCI–BİRİNCİ–DERECEDEN HİDROLİZİNİN HIZ KATSAYISININ BELİRLENMESİ

DIFFERENTIAL SPECTROPHOTOMETRY IN CHEMICAL KINETICS: DETERMINATION OF THE PSEUDO–FIRST–ORDER RATE COEFFICIENT OF METHYL SALICYLATE HYDROLYSIS

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SUMMARY

Differential spectrophotometry was applied to pseudo–first–order hydrolysis of methyl salicylate. Thus, the values of the measured quantity at $t = \infty$ and $t = 0$ were eliminated in calculation of the rate coefficient. Results obtained by this method were compared statistically with those obtained from the classical method.

ÖZET

Diferansiyel spektrofotometri metil salisilatın yalancı–birinci–dereceden hidrolizine uygulandı. Böylece, hız katsayısının hesaplanmasında ölçülen niceliğin $t = \infty$ daki $t = 0$ daki değerleri elendi. Bu yöntemle elde edilen sonuçlar klasik yöntemden elde edilen sonuçlarla istatistiksel olarak karşılaştırıldı.

INTRODUCTION

Differential spectrophotometry is used in analytical chemistry in order to attain higher precision of measurements and higher accuracy in determining various parameters from such measurements (1). This method can be used in chemical kinetics as reported in our previous work (2). Thus, calculation of the rate coefficient of a first–order reaction becomes easier than that of the classical method. The integral rate equation is as follows

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$\ln \Delta A = -kt + constant$

The purpose of this study is to apply differential spectrophotometry to the hydrolysis of methyl salicylate (MS), provided the reference (retarted reaction) and sample (reaction) are exactly identical.

According to other investigators the hydrolysis of MS in aqueous or hydro–alcoholic solutions when the alcohol corresponds to that of the ester function, follows first–order kinetics and when the alcohol does not correspond to that of the ester function, transesterification to produce a second ester may occur and both esters undergo hydrolysis (3, 4). The reaction rate for the first–order hydrolysis of MS was found to be nearly independent of $[OH^-]$ within the $[OH^-]$ range 0.001 – 0.10 mol L^{-1}, and varies with $[OH^-]$ in highly alkaline medium (3, 5).

The reaction was usually followed spectrophotometrically by the disappearance of MS at wavelengths of 332–340 nm region (3, 6, 7, 8).

EXPERIMENTAL

MS was obtained from Merck chemical company (Art 6070). All other chemicals used were of reagent grade. Bidistilled water (1.1 μS) was used throughout the kinetic studies.

The kinetics of hydrolysis of MS was studied by monitoring the disappearance of ester. Shimadzu UV–160A double–beam uv/visible spectrophotometer with CPS–240A temperature controller was used.

A great number of experiments have been carried out in order to select proper concentrations and temperature.

Initial concentration of ester and alkali (NaOH) were 2.1×10^{-4} mol L^{-1} and 0.45 mol L^{-1} respectively in water of 2.5 % methanol. Time dependence spectral changes (A) during a reaction were recorded in repetitive scan mode of the instrument in 260–400 nm region at every 2 minutes. Thus, λ_{max} was determined as 334 nm for MS. Figure 1 shows typical time dependence spectral changes obtained from both Shimadzu and Perkin–Elmer spectrophotometers.

In this paper in order to make comparison two experimental methods were used.

a) *Classical method :* The reactions were carried out at 42.0 ± 0.1 and 37.0 ± 0.1 °C. In the experiments, reaction vessels and quartz cuvettes and solutions were placed in a thermostate for temperature

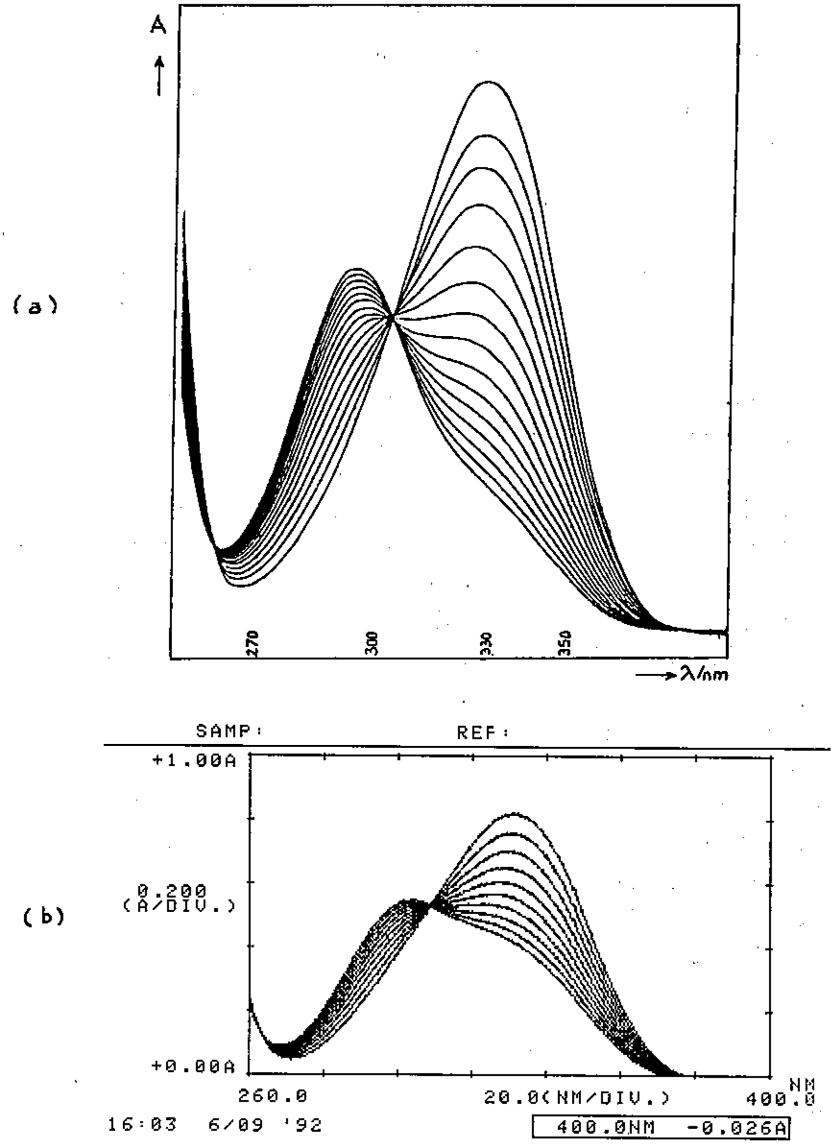

Figure - 1 : Series of spectra recorded for hydrolysis of MS. (a) Obtained from Perkin Elmer and (b) obtained from Shimadzu spectrophotometers. The interval between recordings were 4 and 2 minutes respectively.

equilibration at 42.0 °C (or 37.0 °C). Then the reaction mixture having a total volume 10 mL was prepared (t = 0). An aliquot of 3 mL of the reaction mixture was transferred quickly to the sample cuvette of 1 cm optical path length. The cuvettes were inserted in the cells compartment of spectrophotometer. Absorbance (A) measurements were recorded at every 60 seconds in the kinetic mode of the instrument.

The observed pseudo–first–order rate coefficient were calculated from the following equation

$$\ln\left(A_t - A_\infty\right) = \ln\varepsilon[\,\mathrm{MS}\,]_o - kt$$

A_∞ is the abosrbance of MS at $t = \infty$, and was obtained from the solution of $[\,\mathrm{MS}\,]_o$ / 1000 mol L^{-1} in 0.45 mol L^{-1} NaOH. It was measured as 65.

b) *Differential method :* The method was reported in our previous work (2). It was developed in this paper. Hereafter, instead of two identically prepared reactions initialized at different times, one reaction solution at 6 – 8 °C will be divided into two parts at the beginning. One of which (I) transferred immediately to the reference cuvette at 42 °C was placed in spectrophotometer while the other (II) was kept at 6 – 8 °C (retarded reaction). After 8 – 9 minutes from the initial time of the reaction, solution (II) was poured to the sample cuvette in spectrophotometer and it is allowed to reach the reaction temperature (42 °C) for 10 – 11 minutes. Thus, a retardation was formed between two identical reaction solution by temperature difference. Then the differential absorbance of disappearance of the methyl salicylate was recorded at 335.6 nm (λ_{max}, was determined from the series of spectra of the reaction in A mode of Shimadzu). Figure 2 shows a typical time dependence spectral changes obtained from Perkin–Elmer 5500A spectrophotometer.

RESULTS AND DISCUSSION

Table I gives the measurements of time t and absorbance A values for a typical run of MS hydrolysis. The t values were assumed that they were free from random errors as usually done in chemical kinetics. A (and also ΔA) values were measured with a factor of 1000.

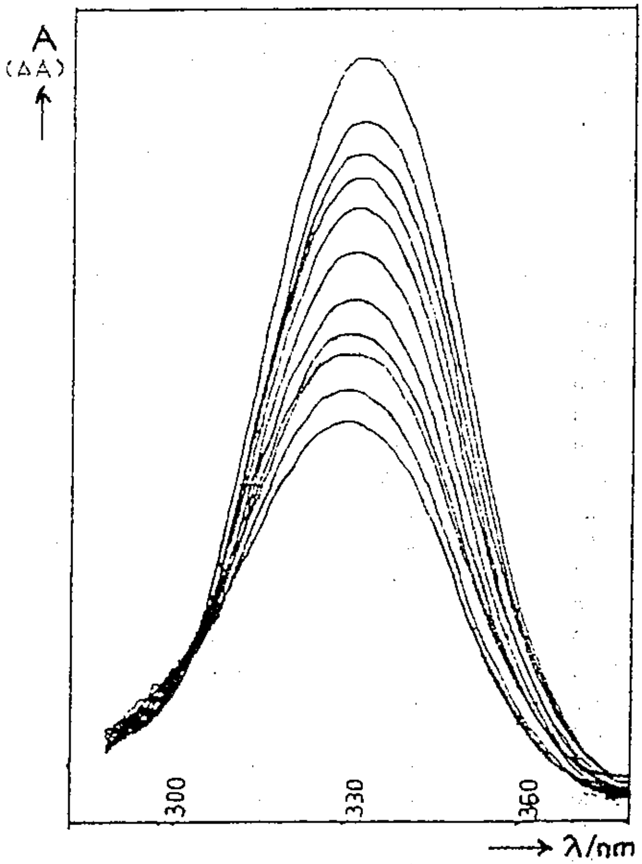

Figure – 2 : Series of differential spectra recorded for hydrolysis of MS against retarded reaction. The interval between recordings was 2 minutes.

The rate coefficient was calculated by weighted least–squares method weighting each point according to $w = (A_t - A_\infty)^2$. For weighting procedure $(A_t - A_\infty)^2$ was chosen since the residuals $[\ln(A_t - A_\infty)_{obs} - \ln(A_t - A_\infty)_{calc}]$ were more randomly distributed about zero than those obtained from the other weighting methods, and the standard deviation of $(A_t - A_\infty)$ was independent of $(A_t - A_\infty)$ (9).

Table – I : Absorbance values of hydrolyis of MS at a series of times and values of $\ln(A_t - A_\infty)$ and $\ln(A_t - A_\infty)$ calculated from the weighted least–squares method for a typical run.

t/sec	$A_t - A_\infty$	$\ln(A_t - A_\infty)$	$\ln(A_t - A_\infty)_{calc}$ $w = (A_t - A_\infty)^2$
360	762	6.636	6.634
420	729	6.592	6.589
480	696	6.545	6.544
540	665	6.500	6.499
600	635	6.454	6.709
660	606	6.407	6.408
720	580	6.363	6.363
780	553	6.315	6.317
840	528	6.269	6.272
900	505	6.225	6.227
960	482	6.178	6.181
1020	460	6.131	6.136
1080	440	6.087	6.091
1140	420	6.040	6.046
1200	403	5.999	6.000
1260	386	5.956	5.955
1320	368	5.908	5.910
1380	352	5.864	5.864
1440	337	5.820	5.819
1500	322	5.775	5.774
1560	309	5.733	5.728
1620	295	5.687	5.683
1680	282	5.642	5.638
1740	271	5.602	5.592
1800	259	5.557	5.547
1860	250	5.522	
1920	239	5.476	
1980	229	5.434	
2040	220	5.394	
2100	211	5.352	
2160	202	5.308	
2220	194	5.268	
2280	186	5.226	
2340	178	5.182	

Figure 3 represents graphically the accuracy with which the data in Table I fit the equation

$$\ln(A_t - A_\infty) = constant - kt$$

First–order rate law is valid at up to 1800 seconds in spectrophotometric method, since the absorbance of the product is not negligible after these seconds; in other words interference becomes more effective. This situation can be seen as a deviation in ln A – *t* line (Figure 3).

Table II includes the calculated rate coefficients and their standard errors of three experiments. Homogeneity of the rate coefficients of three replicate experiments was tested.

$F_{2,69}$ (critical value) = 3.1386 (level 0.05) (10).

$F_{2,69}$ (calculated) = 0.610

So replicate experiments constitute a homogeneous set.

The best values of the rate coefficients and the best estimates for their standard errors were;

Table – II : Calculated values of the rate coefficient assigning $w = (A_t - A_\infty)^2$ and their standard errors.

Run	$10^4 k/s^{-1}$	$10^4 s(k)/s^{-1}$
1	7.559	0.029
2	7.551	0.015
3	7.526	0.020

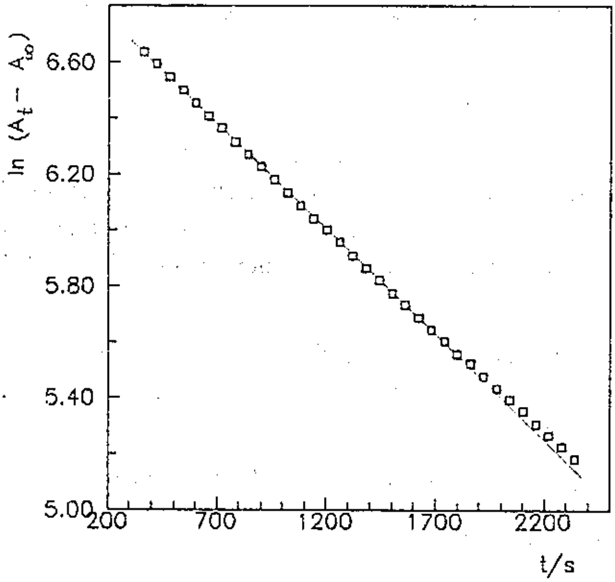

Figure - 3 : A typical plot of ln ($A_t - A_\infty$) against t for hydrolysis of MS. The numerical data are given in Table I.

$\bar{k} = 7.545 \times 10^{-4}s^{-1}$, $s(\bar{k}) = 0.013 \times 10^{-4}s^{-1}$

95% confidence limits for the rate coefficient were found as

$k \cong (7.545 \pm 0.0013 \times 4.303) \times 10^{-4}s^{-1} \cong (7.54 \pm 0,06) \times 10^{-4}s^{-1}$

where Student factor $t_{2,\ 0.05} = 4.3027$ (10)

At 37.0 °C, the results were;

$\bar{k} = 4.84 \text{ X } 10^{-4}s^{-1}$, $s(\bar{k}) = 0.06 \times 10^{-4}s^{-1}$

Thus, activation energy of the reaction was; 72.3 kJ mol^{-1}

Table III represents the time measurements t and differential absorbance measurements ΔA for a typical run of MS hydrolysis.

Table – III : ΔA values of MS hydrolysis at a series of times and values of $\ln\Delta A$ and $\ln\Delta A$ calculated from the weighted least–squares method for a typical run.

t/sec	ΔA	$\ln\Delta A$	$\ln\Delta A_{calc}$ $w = \Delta A^2$
1080	202	5.308	5.310
1140	190	5.247	5.249
1200	179	5.187	5.189
1260	169	5.130	5.128
1320	159	5.069	5.067
1380	150	5.011	5.007
1440	141	4.949	4.946
1500	133	4.890	4.885
1560	125	4.828	4.824
1620	117	4.762	4.764
1680	110	4.700	4.703
1740	103	4.635	4.642
1800	97	4.575	4.582
1860	90	4.500	
1920	84	4.431	
1980	78	4.357	
2040	72	4.277	
2100	67	4.205	
2160	62	4.127	
2220	58	4.060	

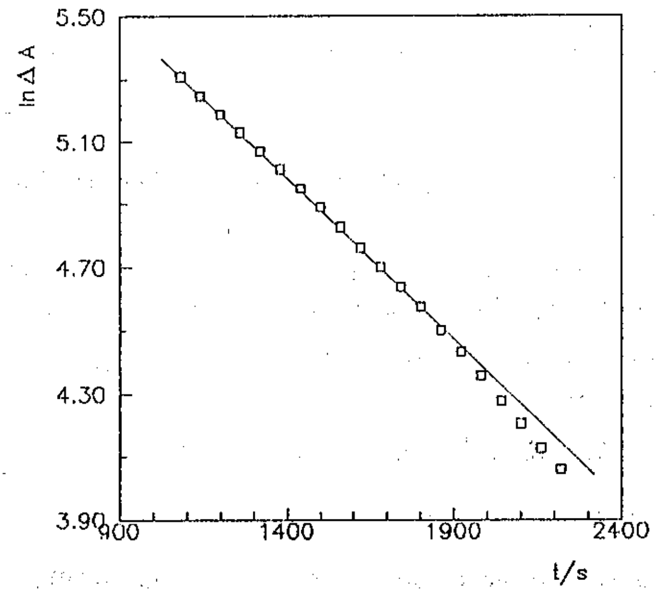

Figure – 4 : A typical plot of $\ln\Delta A$ against *t* for hydrolysis of MS. The numerical data are given in Table III.

Figure 4 shows graphically the accuracy with which the data fit the equation

$$\ln\Delta A = \textit{constant} - kt$$

Here, a deviation was seen again at 1800. second; because of the interference effect of the product.

The rate coefficient was calculated by weighted least–squares method. Each point was weighted by the factor ΔA^2 . The reasons for this choice were the same as before.

The calculated rate coefficients of the three replicate experiments and their standard errors are in Table IV.

Table – IV : Calculated values of the rate coefficient assigning $w = \Delta A^2$ and their standard errors.

Run	$10^4 k/s^{-1}$	$10^4 s(k)/s^{-1}$
1	10.081	0.057
2	9.976	0.039
3	10.121	0.046

F–lest for homogeneity of the rate coefficient of the replicate experiments :

$F_{2,33}$ (critical) = 3.2906, and $F_{2,33}$ (calculated) = 2.6839 (level : 0.05). So replicate experiments constitute a homogeneous set.

The best values of the rate coefficients and the best estimates for their standard errors were :

$$\bar{k} = 10.061 \times 10^{-4} s^{-1}, \; s(\bar{k}) = 0.045 \times 10^{-4} s^{-1}$$

95% confidence limits for the rate coefficient is;

$$k \doteqdot (10.061 \pm 0.045 \times 4.303) \times 10^{-4} s^{-1} \doteqdot (10.06 \pm 0.19) \times 10^{-4} s^{-1}$$

Here, Student factor $t_{2,\ 0.05} = 4.3027$

The results obtained from two methods can be compared with each other statistically :

$F_{1,4}$ (critical) = 7.7086, $F_{1,4}$ (calculated) = 3.39

So, differential method gives results of comparable accuracy to the classical method.

In comparison with the other workers results, a good agreement is found between the values of the rate coefficients and the values of the activation energies of the hydrolysis of MS. For example, the values reported in the literature for 35 °C and ionic strength, $I = 0.4$ mol L^{-1} are $3.42 \times 10^{-4} s^{-1}$ and 70.6 kJ mol^{-1} respectively (3). This value of the rate coefficient is lower than that obtained here, because of the different ionic strength and temperature employed.

Rate coefficient of the reaction weren't determined from the absorbance values of product since the interference of MS band is effective throughout the reaction.

As a result, in order to obtain reliable results the reaction should be followed maximum 1800 seconds at 334 or 335.6 nm in conditions of this study.

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