

First Photolysis of Benzidine Schiff Base in Non Aqueous Solvents

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Abstract

The first photolysis of synthesized Schiff base [Bis-(2-chlorobenzalidene) benzidine] in the presence of various solvents (methanol, acetonitrile and n-hexane) was carried out under UV-light radiation. The data obtained by UV-Visible spectroscopy was used to determine the kinetic parameters of the Schiff base photolysis. It was found that the degradation of Schiff base in all solvents followed a first order reaction. The results show the rate of photolysis depends on the polarity of solvents. The effect of temperature on the photolysis process in methanol has been studied at different temperature ranging from 10°C to 50°C. The activation energy has been determined. The intermediates formed in the Schiff base photolysis processes were detected and identified, using High Performance Liquid Chromatography analytical technique coupled with UV-visible spectrophotometer.

Keywords: Photolysis, Schiff base, Effect of solvents effect of temperature

1. Introduction

Compounds which possess $R-CH=N-R'$ as a general formula are called Imines or Schiff bases and can be efficiently prepared by condensation of an aromatic aldehyde or ketone with an appropriate aromatic amine at an optimum pH of 4-6 using dry alcohol as a solvent (S.A Niazi et al., 2010). Schiff bases have played and continue to play an important role in the development of coordination chemistry (A. A. Osowle, 2008). Schiff bases and their metal complexes are becoming increasingly important in recent years due to their biological activity (F.M. Morad et al., 2007) and their uses as catalysts (J. Zhang, Y. Tang et al. 2005) and as compounds of interesting photoluminescent (V. Papper et al., 2003) and electroluminescent (T. Maindrion et al., 2004) properties.

In spite of the relatively large number of thermal hydrolysis (Z.Huang et al., 2001), thermal decomposition (A. M. Aly et al., 2009) and ionization (J. Donoso et al., 1986) reports on Schiff base compounds, less work was published on photolysis and kinetic studies.

Effect of the medium on kinetics and mechanism of chemical transformations is one of the key problems of the modern physical chemistry. The polarity of a medium and temperature changing play the most important role in this phenomenon. Effects of solvent (R.Kumar and M. Yusuf, 2009) and temperature (K. M. Shareef et al., 2010) on photolysis were extensively studied of organic compounds while comparatively little is known on Schiff-base.

Photolysis is the process that involves the use of light to degrade molecular compounds toward their basic constituents, often carbon dioxide and water. During photolysis, a direct photochemical transformation takes place, when energy from light attacks bonds within a molecular compound, thereby degrading the compound (F. Al-Momani, 2003). The first one is that the organic compound to be eliminated must be able to absorb light in competition with other compounds of the effluent to be treated. The second one is that the organic compounds generate a wide variety of photochemical reactions that can produce products more complex for degradation. In addition, not all the radiation emitted by the source of radiation is fully exploited. Only the radiation absorbed and only a part of this produce chemical changes. This means that some reactions of photodegradation have very slow kinetics (DI Wolfgang, 2006).

A number of papers have been published on the direct photolysis of chemicals in water using the Hg-lamp (K. G. Mostafa, 2007, J.P. Escalanda, 2008, S.T. Ong, 2009). Photochemistry of some 2-butenyl/butyryl-bischromones has been investigated by Kumar and Yusuf (R.Kumar and M. Yusuf, 2009) in benzene and isopropanol-THF (1:1). Photolysis conversion of the bischromones is found to be dependent upon the nature of the intermediate spacer and H-donating capability of the solvent. L. Scrano et al (L. Scrano et al., 2002) reported the direct photolysis of acifluorfen in different solvents (water, methanol, acetonitrile and n-hexane) by UV mercury lamp. On the other hand, J. Sanz-Asensio et al (J. Sanz-Asensio et al. 1999) reported a comparative photolysis kinetic study of ethiofencarb [2-ethylthiomethyl(phenyl)-N-methylcarbamate] in aqueous and non-aqueous media (hexane and methanol). In the present work the first photolysis of Bis-(2-chlorobenzalidene)benzidine have been carried out in different solvent and at different temperature.

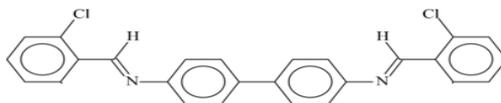
2. Experiment

2.1 Chemicals

Benzidine, 2-chloro benzoic acid and 2-chlorobenzaldehyde supplied by Fluka AG. Methanol and acetonitrile were HPLC grade and purchased from Tedia Company-USA. Other solvents used were obtained from BDH chemicals.

2.2 Preparation of Schiff Base

The Schiff base was prepared by adding 25 cm³ of 2-chlorobenzaldehyde methanolic solution (0.02 mol) to the same volume of methanolic solution of benzidine (0.01 mol). The mixture was stirred for one hour at room temperature (30^o C). The resulting solution was evaporated under vacuum to remove the solvent. The yellow product was collected by filtration, washed several times with methanol and recrystallized from hot methanol and then dried under vacuum. Melting point of Schiff base is 234-237^o C. Chemical structure of Schiff base has been shown in below.



Chemical structure of Bis-(2-chlorobenzalidene)benzidine Schiff base

2.3 Photolysis procedure

The photolysis experiments were carried out at room temperature (30^oC) in a laboratory-made photoreactor including a 35 ml cylindrical photochemical cell. 20ml of solution (50 mg/l of Schiff base in different solvents) was added to the photochemical cell then irradiated immediately by 100-Hg UV lamp (230V, 50Hz and 1 Am, without selector from Osram- Germany). The effect of temperature on catalytic photodegradation was monitored by adjusting the temperature of circulating water between (10^o to 50^o C).

2.4 Analytical methods and instruments

Infrared spectra of the Schiff base were carried out on I.R 300 spectrophotometer from Thermo Mattson -USA by using KBr disk. Melting point was measured on Toshinwal-Electrothermal melting point apparatus. Electronic spectra were recorded in the range 200-300 nm by uv-visible Cesil 3021 spectrophotometer, from England using 10 mm quartz cell. Concentration changes of the Schiff base were determined by monitoring the Schiff base absorption peak at 209nm in methanol, 212nm in acetonitrile and 213nm in n-Hexan from calibration curve. A calibration curve was found to be linear in the range of 0.75 to 100 mg/l with a good correlation ($R^2=0.962$). Circulating thermostat type Julabo F10-Germany was used for controlling the reaction temperature. PerkinElmer series 200 HPLC connected with UV-visible spectrophotometer detector and analytical column (PRT 720041, ET2501814 Nucleosil 120-5 C18 Machereg) was used for detection the Schiff base and some photolysis intermediates with the conditions of *Mobile phase*: Methanol/Water (70:30 v/v), *Flow rate*: 0.1 ml/min, *Detector wavelength*: 254 nm, *Injection volume*: 20 μ l, *Operating temperature*: 30 $^{\circ}$ C

3. Results and discussion

3.1 I.R spectra

The formation of Schiff base is inferred by the appearance of strong band in the IR spectrum at 1618 cm⁻¹ due to azomethine group (A. A. Ahmed and S. A. BenGuzzi, 2008) as shown in Fig. 1.

3.2 Electronic absorption spectra

Ultraviolet-Visible absorption spectral of Schiff base displays absorption bands at 209,252, and 281nm in methanol (206,212 250 and 284 nm in acetonitrile and 203,213, 249 and 285 nm in n-hexane) as shown in Fig. 2, 3 and 4. The 209 nm band of the Schiff base spectrum in methanol (212 nm and 213 nm in acetonitrile and n-hexane respectively) represent the $\pi \rightarrow \pi^*$ transition of substituted aromatic compounds. The $n \rightarrow \pi^*$ transition at 281 nm of Schiff base spectrum in methanol (284 nm and 285 nm in acetonitrile and n-hexane respectively) corresponds to non bonding electron of azomethine group (A. A. Osowle, 2008) as shown in figs. 2,3 and 4.

3.3 Photolysis of Schiff base

The spectra of Schiff base in all solvents indicate that during the photolysis, the intensities of the absorption bands exhibit sudden variation, after which their intensities tend to decrease gradually. Figs. 2, 3 and 4 show a variation in absorption spectra of Schiff base in methanol, acetonitrile and n-hexane respectively at various time intervals of irradiation.

The absorption maximum at 209 nm in methanol, 212 nm in acetonitrile and 213nm of Schiff base spectra are always decreased in intensity with irradiation time indicating the decreasing of Schiff base concentration during the photolysis. Fig. 5 shows the photolysis of 50 mg/l of Schiff base in different solvents at room temperature (30 C°).

3.4 Kinetic studies

The graphical method was employed to predict the order of the reaction. The plot of $\ln C/C_0$ versus irradiant time, (where, C is the concentration of Schiff base at time, C_0 is the initial concentration of Schiff base), gives a straight line behavior, which suggests the first-order kinetics of the photolysis (Ch. Boughelouma and A. Messalhib, 2009) as shown in Fig. 6.

By application of first order equation ($\ln(C/C_0) = -kt$) the reaction rate constants (k) of the photolysis processes are calculated from the slope of the straight line and the reaction half time ($t_{1/2}$) are calculated by equation $t_{1/2} = 0.693/k$ as shown in table 1.

The results in Fig. 6 and table 1 showed that the photolysis of the Schiff base in acetonitrile is faster than the photolysis in n-hexane and slower than the photolysis in methanol. This means that the rate of photolysis of Schiff base increase with increasing the polarity of solvent and consistent with previous photolysis studies (S. K. Pramanikabc and S.Dasb, A. Bhattacharyyaa, 2008). A possible explanation for the higher photolysis rate in polar solvents is due to the contribution of an oxygen independent mechanism which enhanced photolysis reaction (R.Kumar and M. Yusuf, 2009) and polar solvents would achieve better stabilization of the free ions (L. Scrano, 2002).

3.5 Effect of Temperature

The activation emerge (E_a) of photolysis process in methanol was determined after determination of photolysis reaction rate constant at 10, 20,30,40,50°C, the values of the rate constant (k)were plotted in the form $\ln k$ versus $1/T$ (K), as shown in Fig. 7.

The energy of activation (E_a) was determined according to Arrhenius equation $\ln k = \ln A + (E_a/RT)$ (A.Atita, 2008), where A is an empirical constant depending on compound and nonthermal system conditions, R is the universal gas constant ($J/K, mol^{-1}$) and T is the temperature (K). The activated energy of Schiff base photolysis calculated and equal to $0.2399 KJ.mol^{-1}$. The low values of E_a might be considered that the photolysis process in this work is generally temperature independent (N. Mittal, 2009). Other workers also determined low activation energies for catalytic photolysis of organic compounds. (A.Atita, 2008, B. Dabrowski, 2005)

3.6 Photolysis intermediates

Figure.8 shows the HPLC chromatogram of Schiff base before photolysis (time=0) the peak at retention time 2.34 min (peak 1) belongs to the Schiff base as a reactant. After 60 min of photolysis the area of this peak was decreased indicating the decreasing of Schiff base concentration, as shown in fig .9. In fig.9 the new peaks appear in a chromatogram corresponding to the intermediate compounds produce during the photolysis reaction. A peak of retention time 1.51 min was due to 4-hydroxy-2-chlorobenzoic acid (peak 4), while a peak of retention time 1.93 min corresponds to 2-chlorobenzoic acid (peak 2). The formation of 2-chlorobenzoic acid can be explained by considering the oxidation of 2-chlorobenzaldehyd. This suggestion is agreement with that reported by Miray and Nikola (M. Bekbolet, and N. Getoff, 2002), that have reported benzoic acid and 2-chlorobenzoic acid as the main degradation products of 2-chlorobenzaldihyd. While the formation of 4-hydroxy-2-chlorobenzoic acid might be formed by attack of an ·OH radical (M. Bekbolet, and N. Getoff, 2002) on 2-chlorobenzoic acid. It must be pointed out that other intermediates were detected, although attempts to identify them were unsuccessful.

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Table 1. Kinetic parameters for photolysis of Schiff base in different solvents

Solvents	$k(\text{min}^{-1})$	R^2	$t_{1/2}(\text{min})$
Methanol	0.0170	0.9185	40.70
Acetonitrile	0.0128	0.9044	54.14
n-Hexan	0.0098	0.9001	70.71

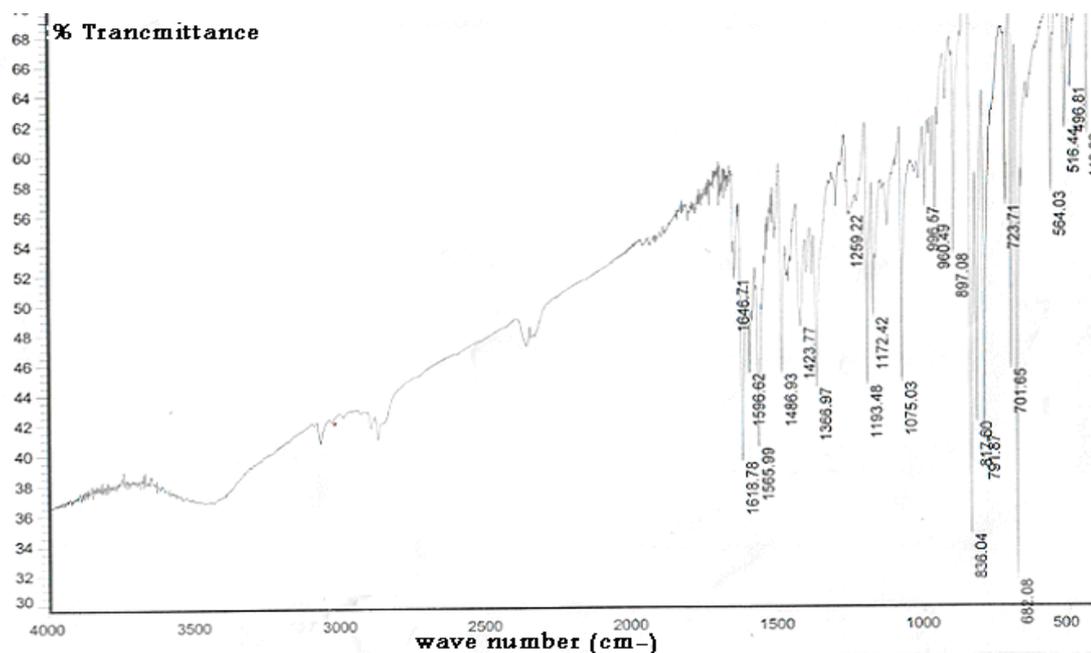


Figure 1. IR absorption spectrum of Schiff base in KBr disk

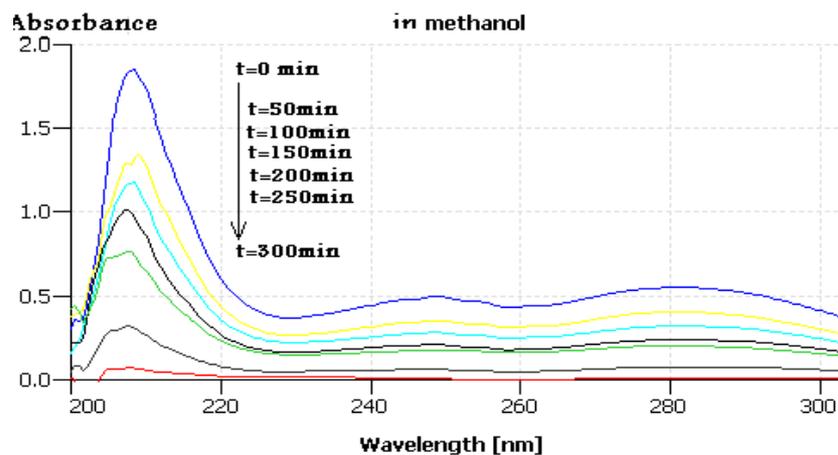


Figure 2. UV-Visible absorption spectra of 50 mg/l of Schiff base in Methanol at various irradiation times

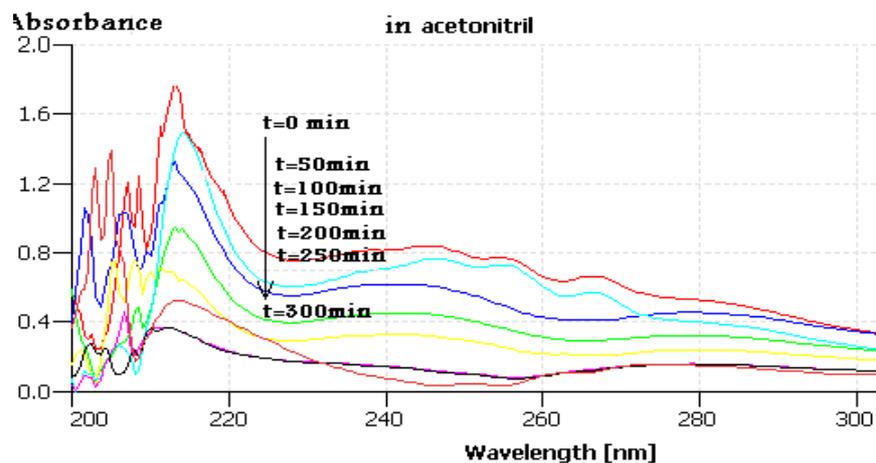


Figure 3. UV-Visible absorption spectra of 50 mg/l of Schiff base in acetonitrile at various irradiation times

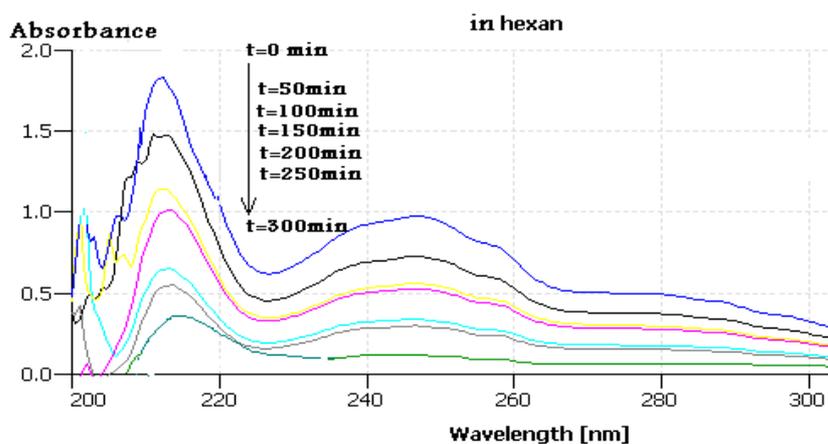


Figure 4. UV-Visible absorption spectra of 50 mg/l of Schiff base in n-hexane at various irradiation times

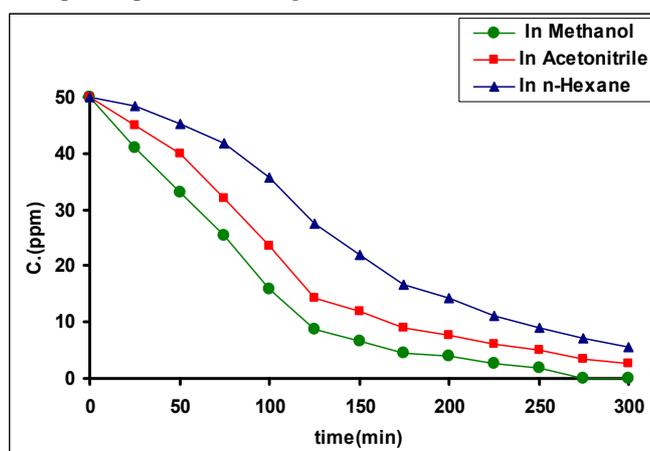


Figure 5. Direct photolysis of 50 mg/l Schiff base in different solvents at room temperature

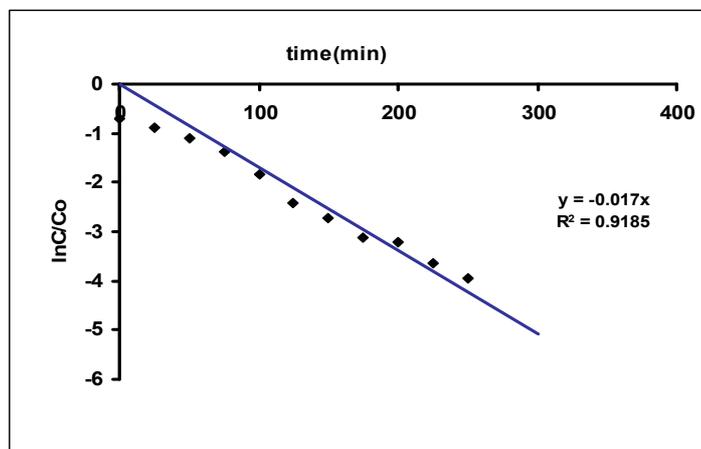


Figure 6. Plotting of $\ln C/C_0$ of Schiff base versus time of photolysis in methanol

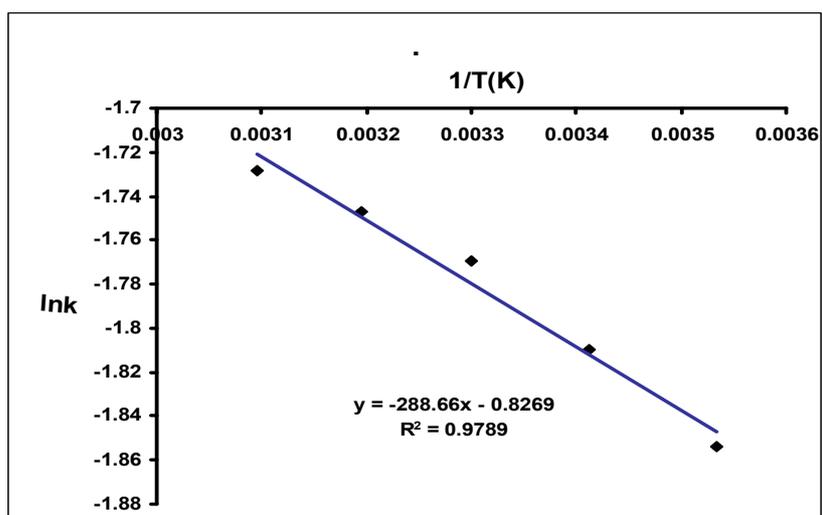


Figure 7. $\ln k$ versus $1/T$ of Schiff base photolysis in methanol

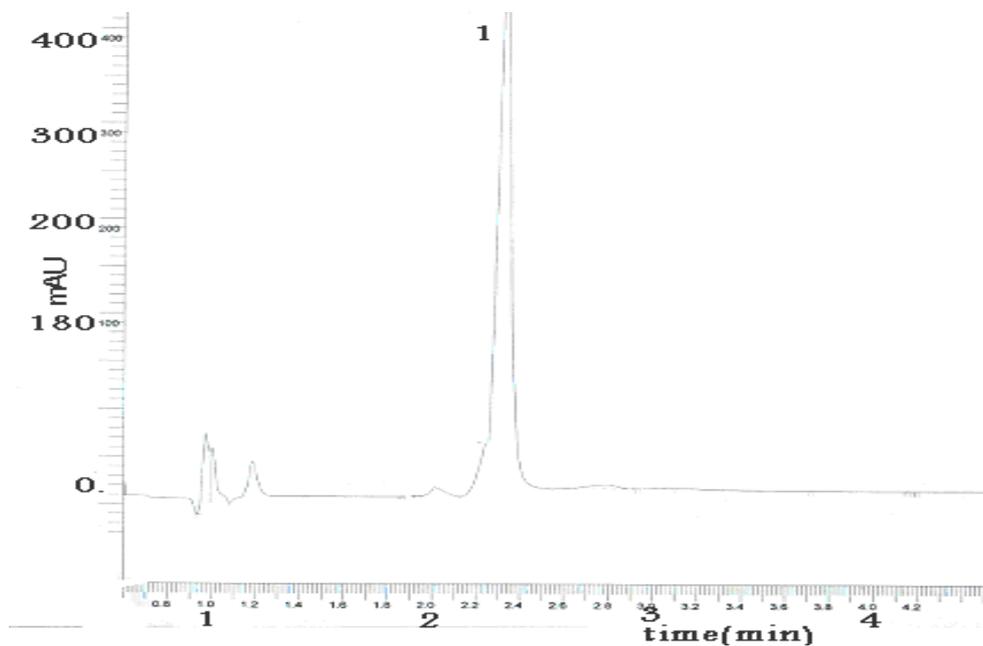


Figure 8. HPLC chromatogram of Schiff base before photolysis

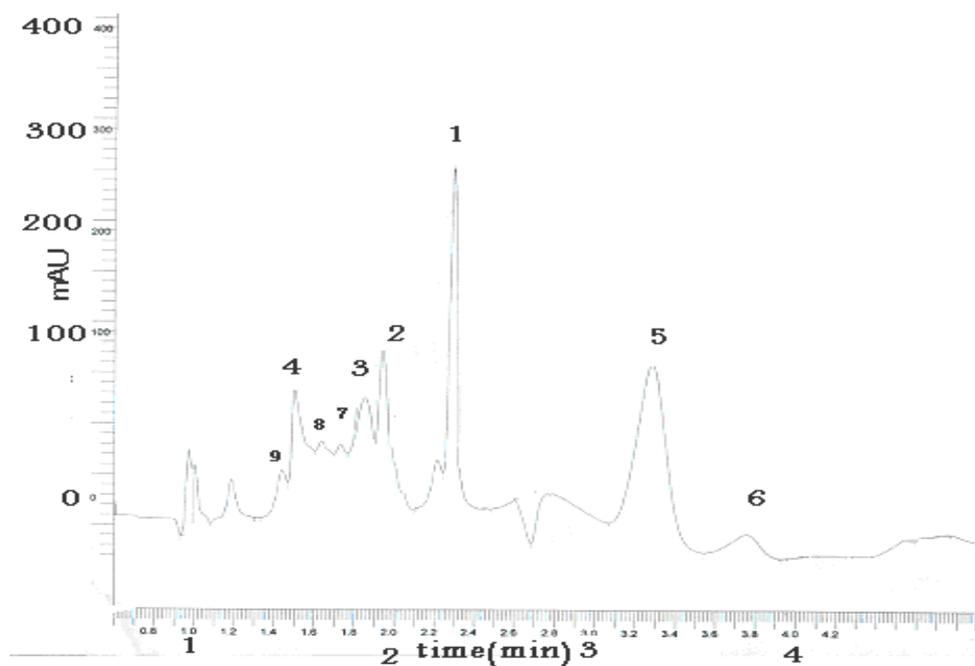


Figure 9. HPLC chromatogram of Schiff base after 60 min of photolysis in methanol