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Kinetics and thermodynamic studies of the chlorination of sultams using a spectroscopic technique

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ABSTRACT

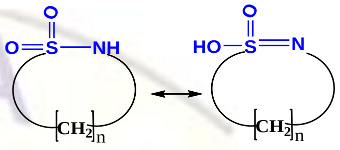
Kinetics and thermodynamic studies of chlorination of N-(p-substituted phenyl) -3,5-dimethyl -1, 1-dioxo-1,2-thiazine ($C_4H_2(CH_3)_2SO_2N\ C_6H_4$-X); {X = H, p-Cl, and p-OCH_3} by using sulfuryl chloride (SO_2Cl_2) in chloroform medium have been investigated by Isolation method the observed rate of chlorination pseudo first order for 1,2-thiazine and SO_2Cl_2 and second order in overall reaction and using spectrophotometric techniques. The reaction rate constant increases with increasing temperature from 273K to 318K. The kinetic and thermodynamic parameters k, E_a, $\Delta H^\#$ and $\Delta S^\#$ have been calculated. The corresponding halogenated 1,2-thiazine has been identified as a product of halogenation. A suitable reaction scheme is proposed and an appropriate rate law is deduced to account for the observed kinetic and thermodynamic data.

Keywords – Chlorination (SO_2Cl_2), Kinetic, Sultam, Spectroscopy, Thermodynamic.

1. INTRODUCTION

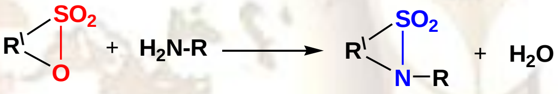
Sulfonamides have long been recognized for their wide range of biological activities[1] and are among the most common causes of allergic reactions of drugs. Recently, much interest has been directed to their cyclic counterparts, the sultams, which also exhibit a vast variety of biological activities. A number of substituted sultams have proven to be useful heterocycles for medical applications[2,3]. As a consequence, chemical syntheses towards sultams have continued to be an attractive topic for intense research[4].

Sultams {1} are inner Sulfonamides in which the S–N bond is part of a ring, the tautomeric forms of sultams, having a sulfur–nitrogen double bond as part of a ring, are called Sultimes {2}. The chemical composition of which corresponds to the general formula[5]:



Sultam {1} Sultime {2}

Unsaturated sultams prepared from the corresponding sultones, (Sultones are intramolecular cyclic esters of hydroxy sulfonic acids) it has surprisingly been found that unsaturated sultones may be condensed with ammonia or primary amines yielding unsaturated sultams. The reaction proceeds in accordance with the general reaction scheme[6]:

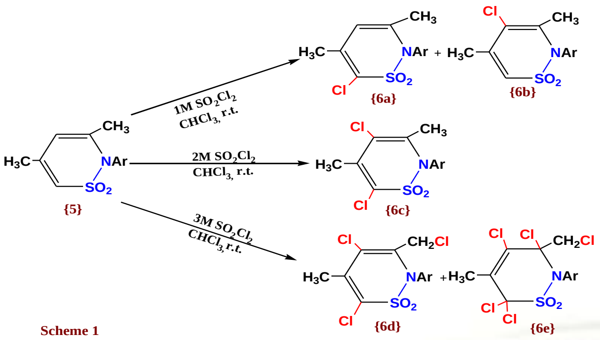


Sultone Sultam

The unsaturated sultams, in accordance with the invention are highly stable and permit further reactions in the sultam ring as well as in the substituents at the sultam nitrogen atom[6]. 1,2-thiazine is a type of sultams, was prepared by mixing of 4,6-dimethyl-1,2-oxathiine-2,2-dioxide{3} with aniline {4} or p-substituted aniline and heated for 1.5 hr., giving N-(p-substitutedphenyl)-3,5-dimethyl-1,1-dioxo-1,2-thiazine {5}[7].

{3} {4} R=H
R=Cl
R=OCH_3
High yield
{5}
Sultam A R=H
Sultam B R=Cl
Sultam CR=OCH_3

1,2-thiazine could be easily chlorinated by using sulfuryl chloride (SO_2Cl_2) in chloroform, using different molar ratio of sulfuryl chloride, to give different chlorinated products {**6a-e**}(scheme 1)[8]:



Scheme 1

Because of our continuing interest in mild reagents for the introducing of halogens into organic molecules and because only limited kinetic and thermodynamic information is available on sultam reactions with Sulfuryl chloride, we found it is important to determine kinetic and thermodynamic parameters of the halogenation reactions of 1,2-thiazine.

2. EXPERIMENTAL

2.1 Chemicals

All chemicals used were of an analytical grade reagent, and methanol (99.9% purity) was purchased from TEDIA Company, Inc. (USA). N,N-Dimethylformamide (DMF) 99.8% from BioSolve. Acetone 99.5%, Chloroform >99.4%, Sulfuryl chloride (SO_2Cl_2) >97% hydrochloric acid (HCl) 97% by Fluka., Aniline 90% , Acetic anhydride 99%, Sulphuric acid and sultone 98% by Sigma Aldrich Co.,4-Chloroaniline, 4-methoxyaniline by Riedel-de Haën, Franç.

2.2 Synthesis of N-(p-substituted phenyl)-3,5-dimethyl-1,1-dioxo-1,2-thiazine ((5)A-C)

A mixture of 0.1mole (16gm) sultone {3} and 0.1 mole (9.1 ml) of aniline or p-substituted aniline were dissolved in 25ml N,N-dimethyl formamide (DMF), the contents reflexed for 1.5hr , then cooled to room temperature and 10ml of (0.1 N) HCl was added to remove the excess of aniline then the precipitate collected by filtration, washed with cold water dried and recrystallized in methanol[9]. The physical properties are shown in table(1).

Table (1): SOME PHYSICAL PRPERTES OF THE COMPOUNDS (SULTAM A, B, C).

Compounds		***para-R p-R***	***Molecular formula***	***M.wt (g/mol)***	***Yield %***	***λmax (nm)***
sultam	A	H	$C_{12}H_{13}NO_2S$	235.303	53	290
	B	Cl	$C_{12}H_{12}NO_2SCl$	269.749	42	260
	C	OCH_3	$C_{13}H_{15}NO_3S$	265.329	49	260

2.3 Experimental techniques and apparatus

The experimental techniques that have been used in kinetics studies to accomplish these measurements are many and varied. The most useful technique that we used in kinetic studies is **UV-Vis spectroscopy:** since the experiment should be done under isothermal condition, the reactor would be immersed in the thermostated liquid bath.

The UV-visible absorption spectra were measured on a Spectroscan 80D instrument spectrophotometer with serial no.:18-1884-01-0113, with UV-spectroscan software, using 1cm matched quartz cells with a home-made cell jacket, made from a thin copper sheet, which was painted by a black dye to minimize the light reflection, connected a thermostated digital circulating bath.

The instrument records the absorbance curve systematically for the product and automatically at fixed cycle time (in sec), between (190-1100)nm. Taking continuous readings until the absorbance remains constant for two hour and this value represents (A_∞). All the experiments were repeated at six different temperatures (273, 283, 293, 298, 303, 318)K, for each reaction.

2.3.1 Typical kinetic experiment of the molar ratio (1:15) (Sultam A : SO_2Cl_2)

The reaction was carried out in a 25ml conical flask, 0.235g (0.001mol, 0.1608mol dm^{-3}) of 1,2-thiazine (Sultam A) and 5ml of chloroform was added by means of micro burette, the flask was placed inside the automatic liquid bath at 298K for thermal equilibration for 30 min before the experiment. The chlorinated agent, sulfuryl chloride (SO_2Cl_2) 1.215ml (0.015 mol, 2.412mol dm^{-3}) was added to the sample solution and quickly mixed then added to the cuvette and capped, the cuvette was inserted into the UV-visible system, It should be mentioned that the wave length range of SO_2Cl_2 is 200-300nm[10], the λ_{max} measured by our spectrophotometer was 260nm in chloroform. Then taking baseline spectrum at full range (190-1100)nm for all the solution mixture to auto zero all the peaks of the reactant solutions, then "start" button was pressed, and the instrument records the absorbance curve systematically for the product, taking continuous readings automatically at fixed cycle time every 600 seconds, until the absorbance remains constant for two hour which represents (A_∞). All the experiments were repeated at six different temperatures (273, 283, 293, 298, 303, 318)K.

A similar experiment was also performed for sultams B and C.

2.3.2 Molar ratio (15:1) (Sultam A : SO_2Cl_2)

The same above experiment was repeated at the inverse molar ratio of reactants changing the concentrations by dissolving 3.529g (0.015mol, 2.952mol dm^{-3}) of 1,2-thiazine (Sultam A) 5ml of chloroform at 298K and the chlorinated agent, sulfuryl chloride (SO_2Cl_2) 81µl (0.001mol, 0.196mol dm^{-3}) was added. The experiment repeated at other five temperatures (273, 283, 293, 303, 318)K, A similar experiment was also performed for sultams B and C.

2.3.3 Molar ratio (1:1) (Sultam A : SO_2Cl_2)

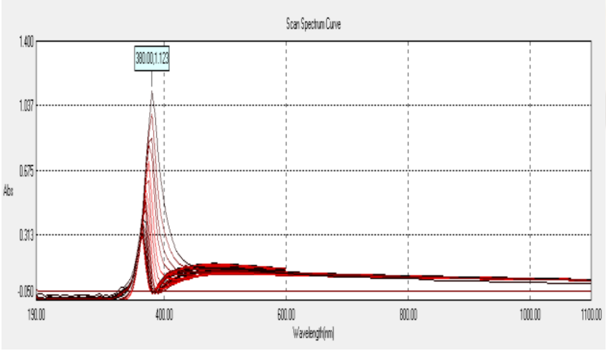
The same experiment was repeated for equal concentrations of reactants by dissolving 0.235g (0.001mol, 0.1968 mol dm^{-3}) of 1,2-thiazine (Sultam A) 5ml of chloroform and the chlorinated agent, sulfuryl chloride (SO_2Cl_2) 0.08ml (0.001 mol, 0.11968mol dm^{-3})was added. The experiments repeated at six temperatures (273, 283, 293, 298, 303, 318)K. A similar experiment was also performed for sultam B and C.

3. RESULTS AND DISCUSSION

3.1 The chlorination using sultam : SO_2Cl_2 (1:15) molar ratio

The chlorination of sultams by sulfuryl chloride in chloroform has been kinetically investigated at six different temperatures with excess sulfuryl chloride ($[SO_2Cl_2] >> [\text{sultam}]$), at constant temperature. The spectral changes, from the start of the reaction toward the completion, demonstrate very clearly how absorbance changes over time for the chlorinated sultam (A) at 380nm, and time course measurement was obtained from the 3-dimensional data, (as shown in two and three dimensional spectrum curves respectively in fig.(1) also for sultam (B) and sultam (C) are shown in the fig. (2) and (3) respectively ,shortly after the peaks begin to appear and increase in intensity as a result of the increase of the formation of the product with time. In this way, time course data freely indicate that no equilibrium occurred at all between the product and reactants within the time period studied.

The variation of absorbance of the product with time for the chlorination of the three sultams (A, B, C) at six different temperatures ranged between (273 to 318)K are shown in fig. (4).



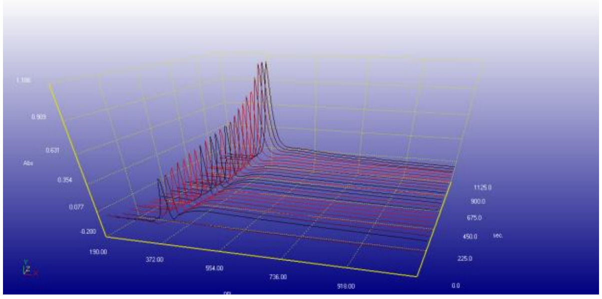


Figure (1): two dimensional and three dimensional spectrums for sultam A at 298K, (1:15) ratio.

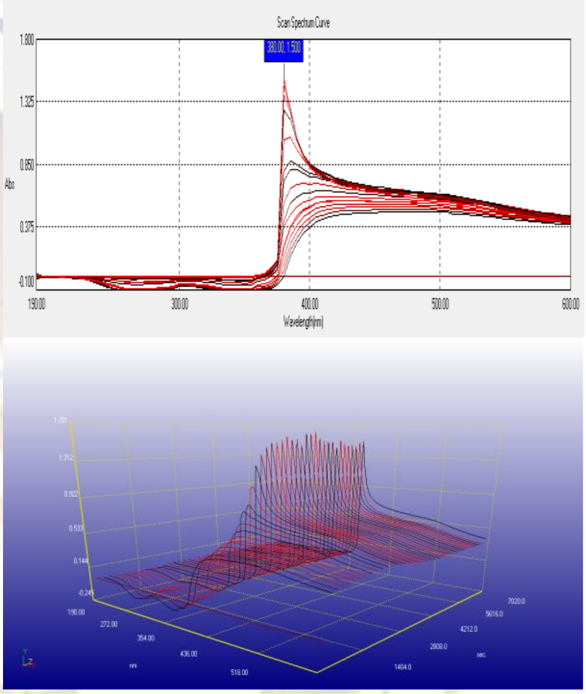
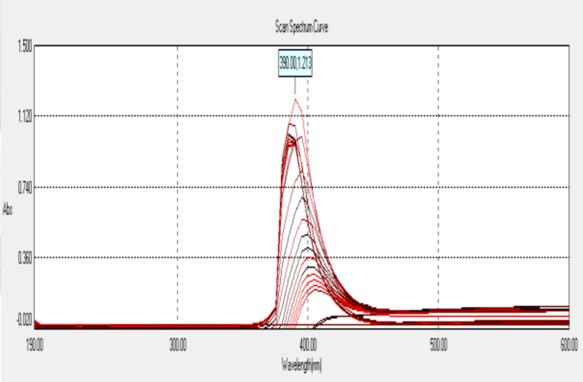


Figure (2): two dimensional and three dimensional spectrums for sultam B at 303K, (1:15) ratio.



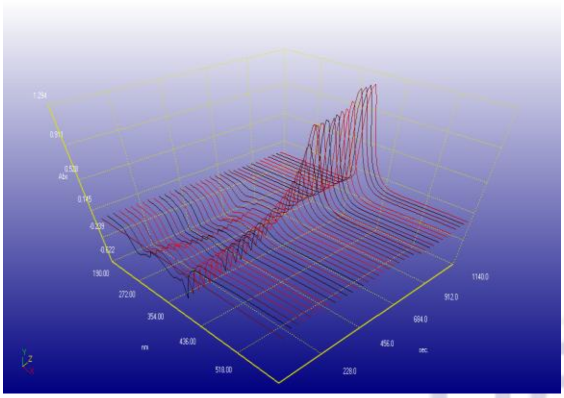
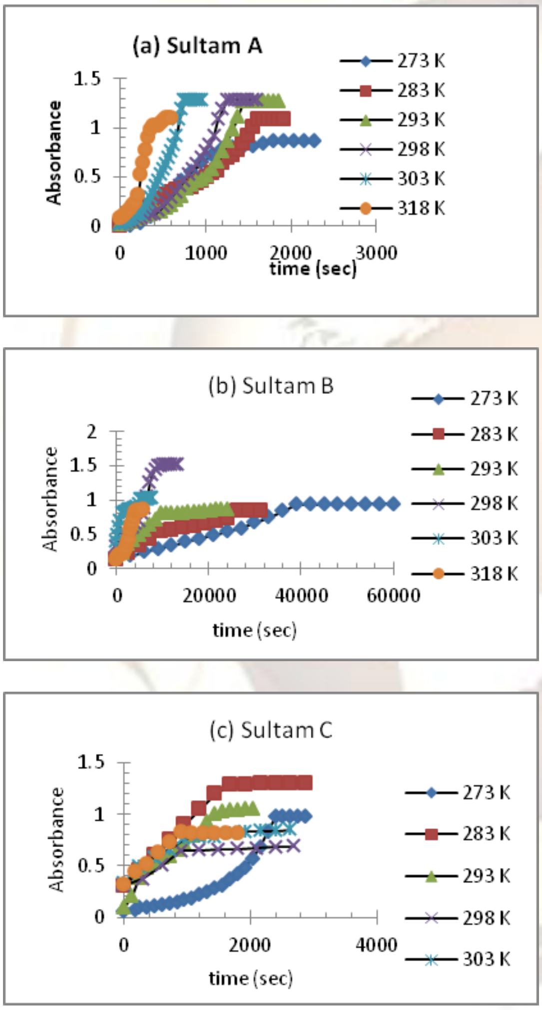


Figure (3): two dimensional and three dimensional spectrums for sultam C at 318K, (1:15) ratio.



Figure(4):Variation of absorbance of the product with time for chlorination of sultams (A, B, C) at different temperature.

The results obtained from the kinetic data for the product of the chlorination of sultams were found to follow pseudo first-order kinetics according to the equation (1). The rate constant values (k) at different temperature were calculated for the product from the pseudo first order equation[10,11]:

$$Ln(A_\infty - A_t) = \ln A_\infty - kt \qquad (1)$$

Where A_0: Absorbance of the product at zero time, equivalent to base line of product.

A_t: Absorbance of the product at any time (t).

A_∞: Absorbance of the product at infinite time (t∞), and also equivalent to the initial concentration of reactant (a).

t: time in sec. k: rate constant of reaction in sec^{-1}

(A∞-At): concentration of product at any time, and also equivalent to remaining concentration of reactant (a-x).

The value of k for each temperature was evaluated from the slope of the linear plots of $\ln(A_\infty - A_t)$ against (t), the data plots are shown in the fig. (5) and the summary of findings of k, $t_{1/2}$, and R^2 are given in the table (2a, b and c), where $t_{1/2}$ is the half-life of the reaction. R^2 is the correlation coefficient which is a measure of the goodness-of-fit of the regression and $0 \le R^2 \le 1$.

3.1.1 Determination of thermodynamic activation parameters

The rate constants for the reaction at the six different temperatures were plotted against 1/T and the activation energy (E_a) was calculated from the slope of the Arrhenius plot (as shown in fig. (6)) which shows a good straight line with the slope of ($-E_a/R$) as in the equation (2):

$$\ln k = \ln A - E_a / RT \qquad (2)$$

From the obtained results of the activation energy E_a, the enthalpy of activation $\Delta H^\#$, entropy $\Delta S^\#$ and Gibbs free energy of activation $\Delta G^\#$ can be obtained using equations[12,13]:

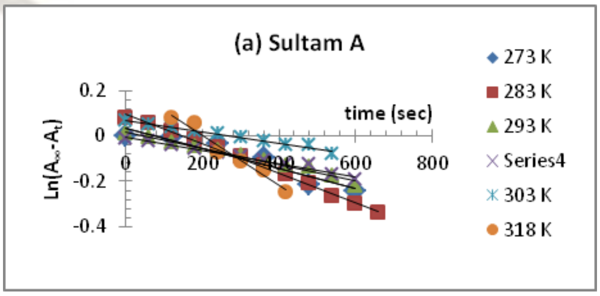
$$\Delta H^\# = E_a - RT \qquad (3)$$

$$A = \frac{eKT}{h} e^{\frac{\Delta S^\#}{R}} \qquad (4)$$

$$\Delta S^\# = R(LnA - Ln(ek_b T / h)) \qquad (5)$$

$$\Delta G^\# = \Delta H^\# - T\Delta S^\# \qquad (6)$$

where k_b= 1.3806*10^{-23} J K^{-1}, h= 6.626*10^{-34} J sec. The Arrhenius parameters, activated enthalpies and entropies obtained from the plotted graphs are tabulated in table (3) and (4).



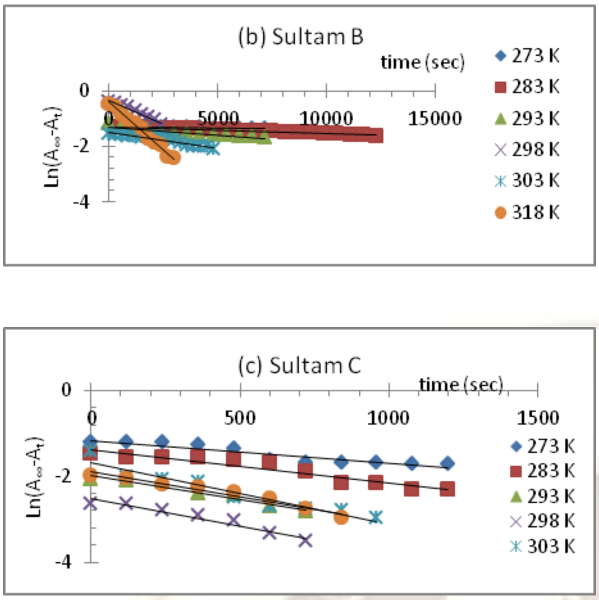


Figure (5): first order plot for the absorbance of the product of sultam with sulfuryl chloride in chloroform using 1:15 molar ratio reactants.

Table (2a): Observed rate constants, for the chlorination of sultam A by SO_2Cl_2 with molar ratio (1:15).

Temp. (K)	$k_{obs} \times 10^{-4}$ (sec^{-1})	$t_{1/2}$ (sec)	R^2
273	6.9	1004.3	0.962
283	9.5	729.4	0.992
293	12	577.5	0.996
298	14	495.0	0.981
303	17	407.6	0.979
318	24	288.7	0.913

Table (2b): Observed rate constants, for the chlorination of sultam B by SO_2Cl_2 with molar ratio (1:15).

Temp. (K)	$k_{obs} \times 10^{-4}$ (sec^{-1})	$t_{1/2}$ (sec)	R^2
273	0.26	26653.8	0.996
283	0.5	13860.0	0.979
293	1	6930.0	0.971
298	3	2310.0	0.978
303	3.4	2038.2	0.969
318	13	533.0	0.988

Table (2c): Observed rate constants, for the chlorination of sultam C by SO_2Cl_2 with molar ratio (1:15).

Temp. (K)	$k_{obs} \times 10^{-4}$ (sec^{-1})	$t_{1/2}$ (sec)	R^2
273	10	693	0.948
283	14	495	0.911
293	18	385	0.939
298	20	346.5	0.951
303	23	301.3043	0.919
318	33	210	0.935

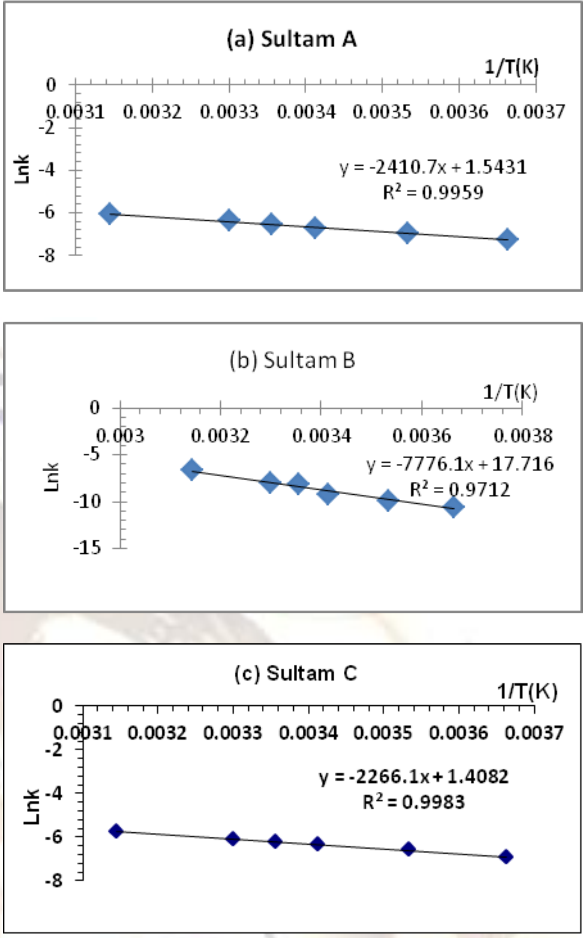


Figure (6): Arrhenius plots for chlorination of sultams (A, B, C) at different temperatures using (1:15) molar ratio of sultam: SO_2Cl_2.

Table (3): Arrhenius parameters and entropies of activation for the chlorination of sultams (A, B, C) using (1:15) molar ratio of sultam: SO_2Cl_2.

Sultam	E_a ($KJ.mol^{-1}$)	R^2	A-factor/ s^{-1}	$\Delta S^{\#}$ ($J.mol^{-1} K^{-1}$) at 298K
A	20.042	0.995	4.679	-240.390
B	64.650	0.971	49426634.66	-105.929
C	18.840	0.998	4.088	-241.512

Table (4): Thermodynamic parameters for the chlorination reaction of sultams (A, B, C) using (1:15) molar ratio of sultam: SO_2Cl_2.

Sultam	Temp. (K)	$\Delta H^\#$ ($KJ.mol^{-1}$)	$\Delta S^\#$ ($J.mol^{-1} K^{-1}$)
A	273	17.772	-239.662
	283	17.689	-239.961
	293	17.606	-240.249
	298	17.564	-240.390
	303	17.523	-240.528
	318	17.398	-240.930
B	273	62.380	-105.200
	283	62.297	-105.499
	293	62.214	-105.788
	298	62.172	-105.929
	303	62.131	-106.067
	318	62.006	-106.469
C	273	16.570	-240.783
	283	16.487	-241.082
	293	16.404	-241.371
	298	16.362	-241.512
	303	16.321	-241.650
	318	16.196	-242.052

3.1.2 Interpretation of the overall kinetic and thermodynamic results

The kinetic results for the reaction between sulfuryl chloride with different substituted sultams as summarized previously in tables (2a, b, and c) shows that the reactions are forward processes, since equilibrium not observed during kinetic runs and no compounds other than the product were even detected during kinetic measurements. Temperature changes in the range of (273-318)K increases the rate of the reaction of compounds studied as shown in tables (2a, b and c) which means that the reaction rate is temperature dependent. The increase of the absorbance of the product with time with time as shown from the fig. (4) shows that as the temperature increase, the amount of molecular interactions also increase and the reaction more quickly goes to product. Typical plots show excellent fit to equation (1) and were always linear, as shown in fig. (5) thus the assumption of pseudo-first order reaction is fully proved.

k-value calculated in table (2) are very low i.e. the reactions are slow (require one hour or more to be complete) specially in sultam B due to the p-chlorosubstituent at the benzene ring, because of the high electronegativity of chlorine which affect as electron withdrawing group, which slows down the reaction giving rise to smaller k-values. The comparison of the rate and the time of the chlorination reaction of unsubstituted sultam(A) with other two different substituted sultams (B and C) at 273K is:

1- The unsubstituted sultam (X=H) was taken as a reference reaction rate for comparison ($t_{1/2}$ = 1004.3 sec.).
2- When (X= p-Cl) which is electron withdrawing group, it reduced electron density at the reaction center. As a result the rate of reaction decreased, i.e. $t_{1/2}$ increased ($t_{1/2}$ =26653.8 sec.).
3- When (X= p-OCH_3) which is electron donating group, thus enrich electron density of the reaction center of the formed activated complex. The rate of reaction increased, i.e. $t_{1/2}$ decreased ($t_{1/2}$ = 693 sec.).

The energy difference between the reactants and the transition state, which is known as activation energy E_a which calculated from the fig. (6) were low for sultam C and A (17.6 and 20.0)KJ/mol respectively which means that the easier for the reaction to occur, especially for the sultam C which has p-OCH3 substituent at benzene ring which is electron donating group which makes the reaction easier and faster, while the sultam B has E_a=64.6KJ/mol the harder it is for the reaction to occur. When the temperature increase, the amount of molecular interactions increases, then the internal energy of the system rises, according to the equation (3) when the internal energy E_a increase then the $\Delta H^\#$ will increase, as shown in table (4).

The pre-exponential factor (A) values were directly proportional to (E_a) in general as represented and expected[14,15]. It represents the frequency of collisions between reactant molecules. The abnormal low values of (A) were explained according to the transition state theory[13], by the decrease in partition function of the transition state, Q^*_{AB}, and the increase in the partition functions of the reactants, Q_A and Q_B, according to the equation (7):

$$A = \frac{KT}{h} * \frac{Q^*_{AB}}{Q_A Q_B} \qquad (7)$$

Which indicate the more rigid configuration with less degree of freedom for the activated complex which has a simpler configuration than the reactant molecules and low $\Delta S^\#$ values in equation (4). The low negative values of $\Delta S^\#$ as shown in table (3) and (4), which indicates the more rigid configuration with less degree of freedom for the activated complex than those of the reactant molecules.

1- $\Delta S^\#$ for the reaction between SO_2Cl_2 and unsubstituted sultam (X=H) equal to -240.390 $J.K^{-1}.mol.^{-1}$ is considered as a reference for comparison with the substituted sultam.
2- (X = Cl) the presence of electron withdrawing group lead to higher value of $\Delta S^\#$ = -105.929 $J.K^{-1}.mol.^{-1}$, causes to a less aligned and unstable transition state.
3- Low value of $\Delta S^\#$ = -241.512 $J.K^{-1}.mol.^{-1}$ for (X= OCH_3) for electron donating

groups, which cause increasing electron density at the reaction center which allow for relatively better attack of the SO_2Cl_2 to obtained a more stable transition state.

3.2 The chlorination using sultam : SO_2Cl_2 (15:1) molar ratio

All spectra of the products that were obtained by treatment of sultam: SO_2Cl_2 as 15:1 molar ratios were the same as those of the starting sultam, since the small amount of chlorinated product relative to large amount of the unreacted sultam disappears, giving no detectable products.

3.3 The chlorination using sultam : SO_2Cl_2 (1:1) molar ratio

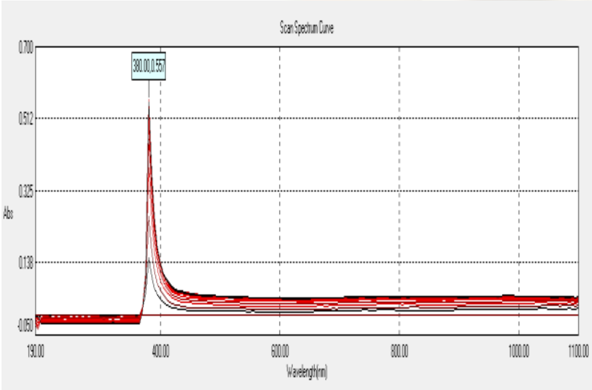
In the chlorination of sultams; using 1:1 molar proportion of sultam and SO_2Cl_2, the measurement of reaction rates was investigated by the rate at which products appear at a particular temperature. The 2 dimensional and 3 dimensional absorption spectra representation of the results of kinetic measurement for sultams at six different temperatures (273-318)K are shown in the fig. (7) to (9), and the variation of absorbance with time are shown in the fig. (10). The Absorbance of the product increase with time and this indicate that no equilibrium occurred between the product and reactants during the studied period of time. The results obtained from the kinetic measurements according to the rate law can be expressed by the equation (8):

$$\frac{d[product]}{dt} = k[SO_2Cl_2][Sultame] \qquad (8)$$

The reactions were determined as second order equation; first-order with respect to each reactant and can be described by equation (9)[16-18]:

$$\frac{A_t}{A_\infty(A_\infty - A_t)} = kt \qquad (9)$$

Which means that the plot of $A_t/(A_\infty(A_\infty - A_t))$ with the time (t) has a slope (k) which is the second order rate constant, the plots show excellent fit to the second order equation as shown in fig. (11) and the data are tabulated in the table (5a,b,c).



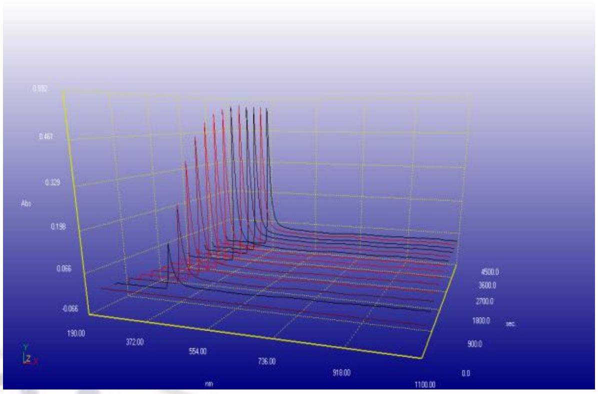
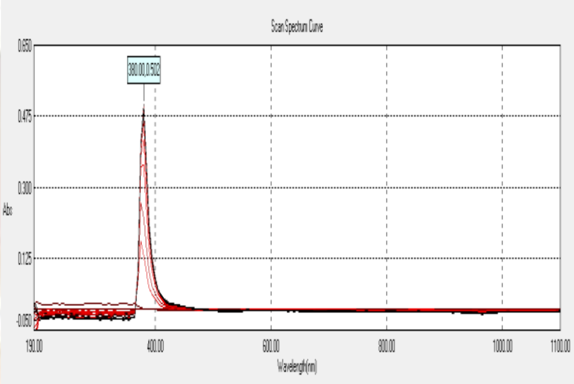


Figure (7): two dimensional and three dimensional spectrums for sultam A at 298K, (1:1) ratio.



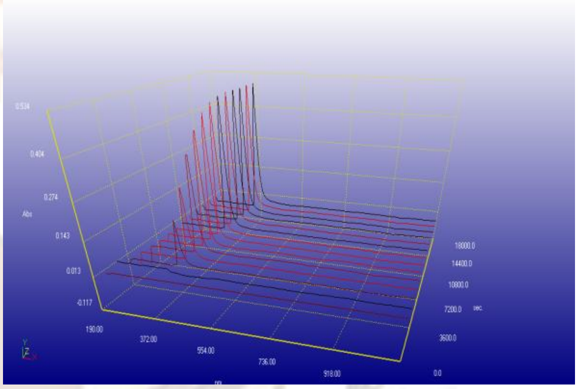
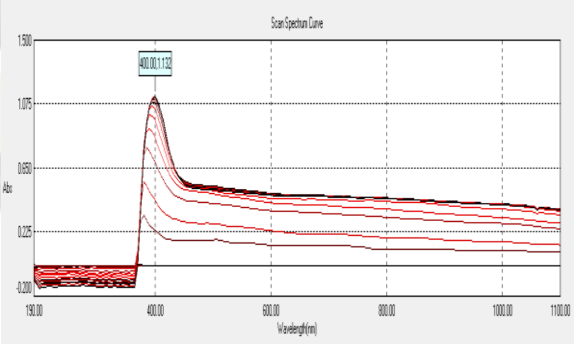


Figure (8): two dimensional and three dimensional spectrums for sultam B at 298K, (1:1) ratio.



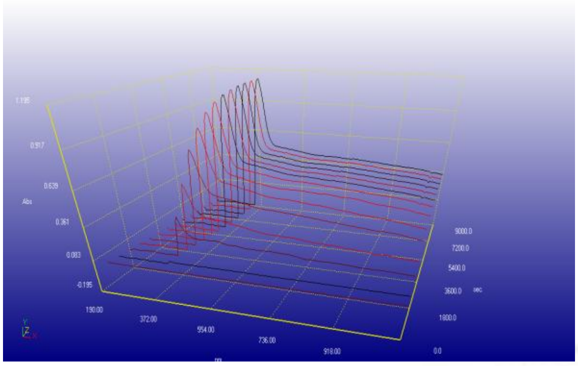


Figure (9): two dimensional and three dimensional spectrums for sultam C at 298K, (1:1) ratio.

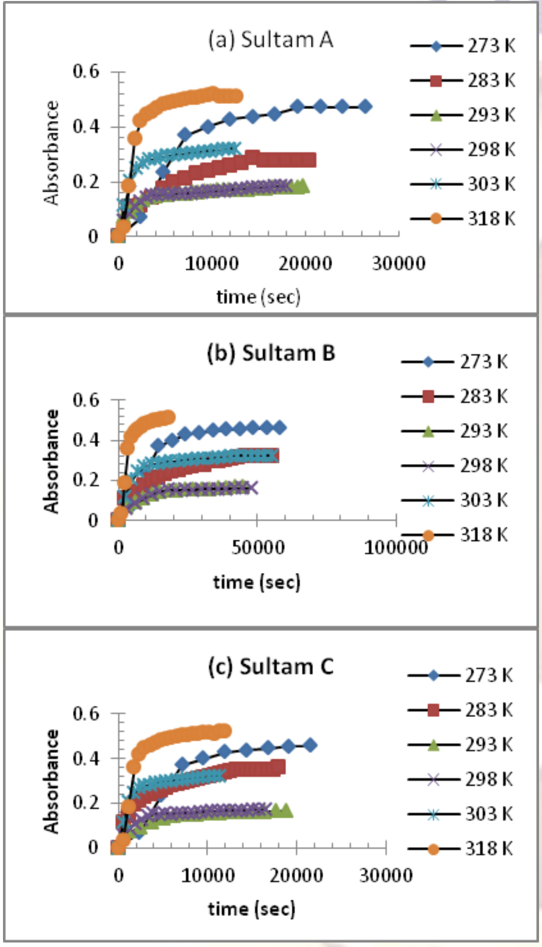
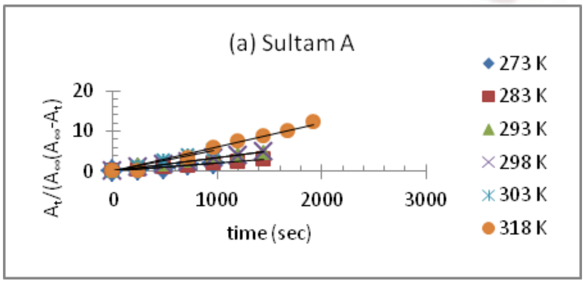


Figure (10): Variation of absorbance of the product with time for chlorination of sultams (A, B, C) at different temperatures using (1:1) molar ratio of sultam: SO_2Cl_2.



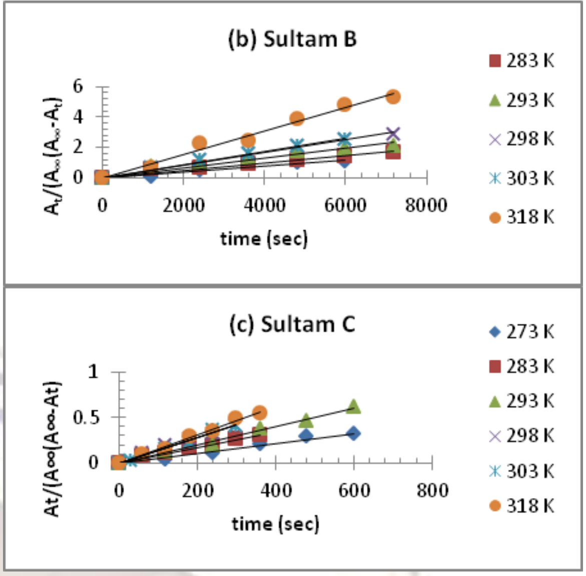


Figure (11): second order plot for the absorbance of the product for chlorination of sultams (A, B, C) at different temperatures using (1:1) molar ratio of sultam: SO_2Cl_2.

Table (5a): Observed rate constants, for the chlorination of sultam A with SO_2Cl_2.

Temp. (K)	**k_{obs}×10^{-4} ($sec^{-1}.L.mol.^{-1}$)**	**$t_{1/2}$ (sec)**	**R^2**
273	5	10162.6	0.929
283	7	7259.001	0.959
293	9	5645.89	0.974
298	10	5081.301	0.939
303	12	4234.417	0.955
318	18	2822.945	0.938

Table (5b): Observed rate constants, for the chlorination of sultam B with SO_2Cl_2.

Temp. (K)	**k_{obs}×10^{-4} ($sec^{-1}.L.mol.^{-1}$)**	**$t_{1/2}$ (sec)**	**R^2**
273	1.6	31758.13	0.957
283	2.4	21172.09	0.946
293	3.4	14945	0.915
298	4	12703.25	0.982
303	5	10162.6	0.959
318	7.4	6866.623	0.981

Table (5c): Observed rate constants, for the chlorination of sultam C with SO_2Cl_2.

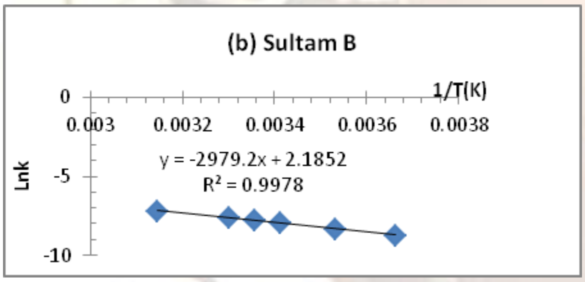
Temp. (K)	**k_{obs}×10^{-4} ($sec^{-1}.L.mol.^{-1}$)**	**$t_{1/2}$ (sec)**	**R^2**
273	6	8468.835	0.948
283	7.8	6514.488	0.946
293	10	5081.301	0.915
298	11	4619.364	0.933
303	13	3908.693	0.959
318	18	2822.945	0.932

Figure (12): Arrhenius plots for chlorination of sultams (A, B, C) at different temperatures using (1:1) molar ratio of sultam: SO_2Cl_2.

Sultam	E_a (KJ.mol^{-1})	R^2	A-factor (s^{-1}.L.mol^{-1})	ΔS$^{\#}$ (J.mol^{-1} K^{-1}) at 298K
A	20.190	0.995	3.629	-242.501
B	24.769	0.997	8.892	-235.052
C	17.629	0.997	1.400	-250.421

Table (6): Arrhenius parameters and entropies of activation for the chlorination of sultams (A, B, C) using (1:1) molar ratio of sultam: SO_2Cl_2.

Sultam	Temp. (K)	ΔH$^{\#}$ (KJ.mol^{-1})	ΔS$^{\#}$ (J.mol^{-1} K^{-1})
A	273	17.920	-241.772
	283	17.837	-242.072
	293	17.754	-242.360
	298	17.712	-242.501
	303	17.671	-242.639
	318	17.546	-243.041
B	273	22.499	-234.323
	283	22.416	-234.622
	293	22.333	-234.911
	298	22.291	-235.052
	303	22.249	-235.190
	318	22.125	-235.592
C	273	15.360	-249.692
	283	15.276	-249.992
	293	15.193	-250.280
	298	15.152	-250.421
	303	15.110	-250.559
	318	14.985	-250.961



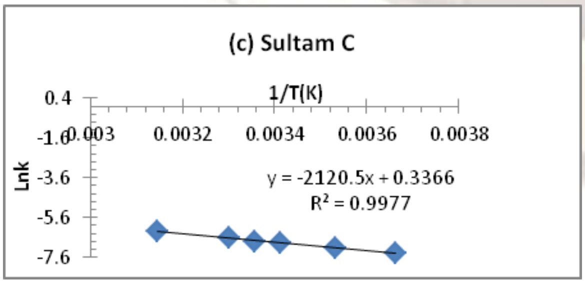


Table (7): Thermodynamic parameters for the chlorination reaction of sultams (A, B, C) using (1:1) molar ratio of sultam: SO_2Cl_2.

3.3.1 Interpretation of the overall kinetic and thermodynamic results

The equi molar ratio of reactants was carried out at different temperatures and the tables (5a,b,c)) shows that the rate of the reaction of studied compounds increases with increasing the reaction temperature; as in plots (3.16) which show excellent linear fit to a second order equation; The rate constant k-values are low, for example comparing k-values at 298K for three sultams show:

1- Chlorination of unsubstituted sultam A using equi molar proceed slowly (k =10 sec^{-1} L mol^{-1}) ($t_{1/2}$ =5081.301sec).

2- The reaction of SO_2Cl_2 with sultam (B) (X= p-Cl) is very slow as compared with unsubstituted sultam (A) this is due to the electron withdrawing effect of chlorine which reduces electron density at the reaction center as a result k decreased (k =4 sec^{-1} L mol^{-1}) and $t_{1/2}$ increased ($t_{1/2}$ =12703.25 sec).

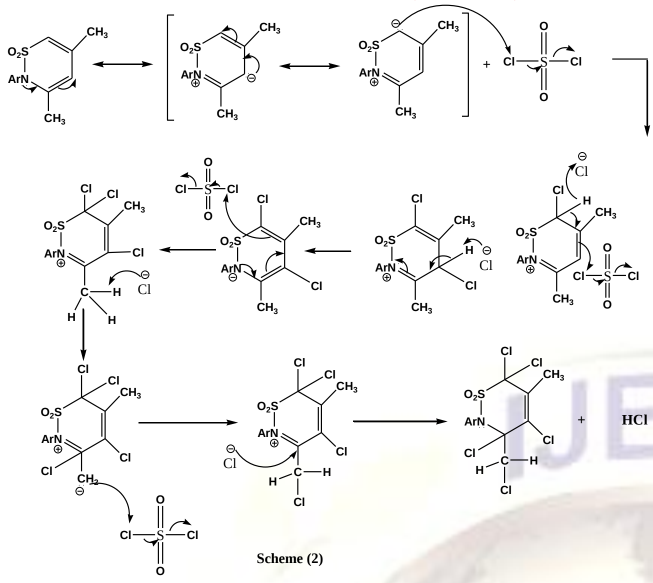
3- When (X = p-OCH_3) which is electron donating group, which increases electron density of the reaction center and the rate of reaction increases (k =11 sec^{-1} L mol^{-1}), decreasing $t_{1/2}$ ($t_{1/2}$=4619.364 sec).

The activation energy obtained from the fig. (12) and tabulated in the table (6) indicates that the energy difference between the reactants and the transition state for sultam (B) is relatively high (E_a= 24.769 KJ.mol.$^{-1}$) in the presence of electron withdrawing group (p-Cl) makes the reaction harder to occur, and needs more energy. While the presence of (p-OCH_3) in sultam C electron donating group makes the reaction easier and faster to occur (E_a=17.629 KJ.mol^{-1}) as compared with unsubstituted sultam A (E_a=20.190 KJ.mol^{-1}). All ΔH$^{\#}$ values are positive (endothermic) means these reactions are consume energy in its process.

The pre-exponential factor (A) value are very low this is explained; according to the transition state theory; by the decrease in partition function of the transition state, Q^*_{AB}, and the increase in the partition functions of the reactants, Q_A and Q_B, according to the equation (7) this indicates the more rigid configuration with less degrees of freedom for the activated complex. The negative value of ΔS$^{\#}$ as shown in tables (6) and (7) indicate the more rigid configuration with less degree of freedom for the activated complex than those of the reactant molecules.

3.4 Reaction mechanism

With the assumption that 1,2-thiazine are nucleophilic, with high electron density, under the influence of the attacking sulfuryl chloride molecule, the 1,2-thiazine molecule is polarized as indicated in the scheme (2), and negative carbon (nucleophile) attacks positively polarized chlorine to produce the carbonium ion, the carbonium ion may lose a proton instead[19,20].



Scheme (2)

4. CONCLUSION

The proposed experimental techniques that have been used in kinetics and thermodynamic studies are quite simple and free from rigid experimental conditions and are characterized by wide linear dynamic ranges and high sensitivity. The importance of the present investigation is to demonstrate the possibility of using a modern in situ spectroscopic method (UV-Vis spectroscopy) to investigate these reaction kinetics.

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REFERENCES

[1] C. Hansch, and P.G. Sammes, *Comprehensive Medicinal Chemistry* (Pergamon press, Oxford, 1990).

[2] P. R. Hanson, D. A. Probst, R. E. Robinson, and M. Yau, *Tetrahedron let.* 40, 4761, 1999.

[3] P.J. Seyden, *Chiral Auxiliaries and Ligands in Asymmetric synthesis*, (Wiley, New York, 1995).

[4] R.C. Brown, J.L. Castro, and J-D Moriggi, *Tetrahedron Let.* 41, 3681, 2000.

[5] A. Jenkins, *IUPAC compendium of chemical Terminology*, 2nd Ed. 67, 1370, 1995.

[6] H. Burckhardt, T. Bonner, Bonu, Germany, *U.S. Pattent. No. 2,917*,512, Dec.15, 1959.

[7] F. Hans, D. Beeck, and H. Tummes, Duisburg-Meiderich, Germany, *U.S. pattent. No. 2,866*,786, Dec. 30 (1958).

[8] Fanghenel E., Mohammed H., Richter A.M. and Radeglia R. *Journal of Practical Chemestry, 326*, 545, 1984.

[9] R.R. Braim, *synthsis of some derevatives of the Brominated 1,2-thiazines using ultrasound technique*, "M.Sc. Thesis", Salahaddin University, College of Science Chemistry Department, 1998.

[10] A.P. Uthman, P.J. Demlein, T.D. Allston, M.C. Withiam, M.J. McClements, and G.A. Takacs, *J. Phys. Chem.*, *82*, 2252, 1978.

[11] A. Semnani, H. R. Pouretedal, and M. H. Keshavarz Bull. *Korean Chemical Society, 27, 6*, 2006.

[12] G.M. Barrow. *physical chemistry* (McGrow Hill Inc), 4th Ed., 1979.

[13] B.G. Gowenlock, *Quart. Rev.*, 140, 133 1960.

[14] R.W. Missen, Ch. A. Mims, and B. A. Saville; *Introduction to chemical reaction engineering and kinetics*, 1998.

[15] Ch. G. Hill, *An introduction to chemical engineering kinetics and reactor design* John Wiley and Sons New York, 1977.

[16] P.W. Atkins *Physical chemistry*, (Oxford University Press, USA 5th Ed., 1995).

[17] K.J. Laidler A glossary of terms used in chemical kinetics, including reaction dynamics *Pure & Applied Chemistry, 68, (1)*, 1996, 149-192.

[18] S. Alberty, J. Robert and A. Robert *Physical chemistry* (John Wiley and songs, Inc. New york, 3rd edition, 2001).

[19] E. Earl Royals *Advanced organic chemistry* (prentice Hall United States America, 1961)

[20] A.E. Shchekotikhin, Y.N. Luzikov, Y.B. Sinkevich, V.N. Buyanov, and M.N. Preobrazhenskaya, Heterocyclic analogs of 5,12-naphthacenequinone 7*. Synthesis of naphtha-[2,3-f] isatin-5,10-Dione derivatives', *chemistry of Heterocyclic compounds, 44(10)*, 2008, 1245-1249.