

Kinetics and Thermodynamic Studies of the Iodination of Sultams Using A Spectroscopic Technique

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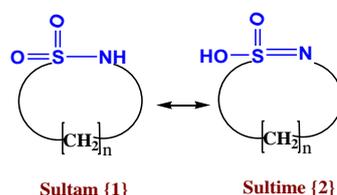
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Abstract - Kinetics and thermodynamic studies of iodination of sultams: *N*-(*p*-substituted phenyl)-3,5-dimethyl-1,1-dioxo-1,2-thiazine ($C_4H_2(CH_3)_2SO_2 N C_6H_4-X$); {*X* = H, *p*-Cl, and *p*-OCH₃} by using iodine monochloride (ICl) in chloroform medium have been investigated by Isolation method the observed rate of iodination, pseudo first order for 1,2-thiazine and ICl 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*, ΔH^\ddagger and ΔS^\ddagger 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.

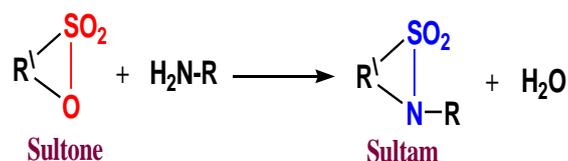
Keywords - Iodination (ICl), Kinetic, Sultam, Spectroscopy, Thermodynamic.

I. 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]:



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]:



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-oxathiane-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}^[7,8].

2.3.1 Typical Kinetic Experiment Of The Molar Ratio (1:15) (Sultam A : ICl)

The reaction was carried out in a 25ml conical flask, 0.235g (0.001mol, 0.0927mol 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 iodinated agent, (ICl) 0.7855ml (0.015mol, 1.39mol 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 λ_{max} measured for the ICl was 345nm in chloroform^[12-13]. 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. similar experiment was also performed for sultams B and C.

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

Using concentrations by dissolving 3.529g (0.015mol, 1.492mol dm⁻³) of 1,2-thiazine (Sultam A) 10ml of chloroform at 298K and the iodinating agent, (ICl) 0.0513ml (0.001mol, 0.0994mol dm⁻³) was added.

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

Using concentrations by dissolving 0.235g (0.001mol, 0.0994mol dm⁻³) of 1,2-thiazine (Sultam A) 10ml of chloroform at 298K and the iodinating agent, (ICl) 0.0523ml (0.001mol, 0.0994mol dm⁻³) was added.

III. RESULTS AND DISCUSSION

3.1 The iodination using sultam : ICl (1:15) molar ratio

Iodination of sultams (A, B and C) were investigated under six temperatures in the range (273-318K), and for each temperature, the time course measurements was followed toward the completion of the reactions, as shown in 2 and 3 dimensional spectra figs.(1) to (3) respectively.

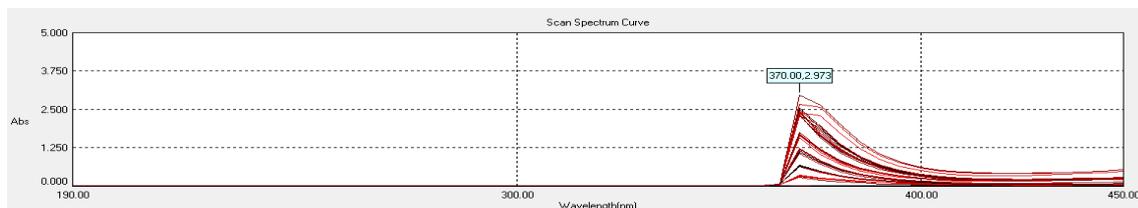


Figure (1)a: two dimensional spectrum for sultam A at 283K, (1:15) molar ratio of (sultam:ICl).

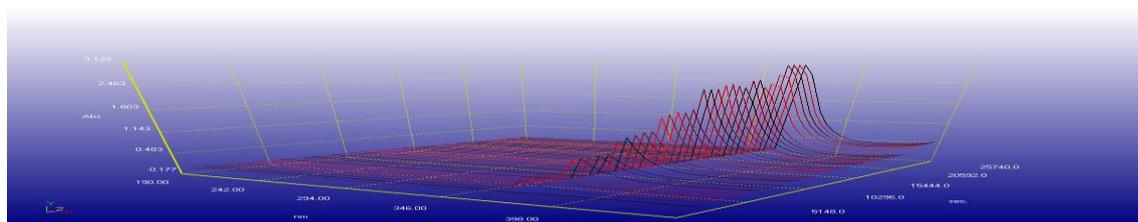


Figure (1)b: three dimensional spectrum for sultam A at 283K, (1:15) molar ratio of (sultam:ICl).

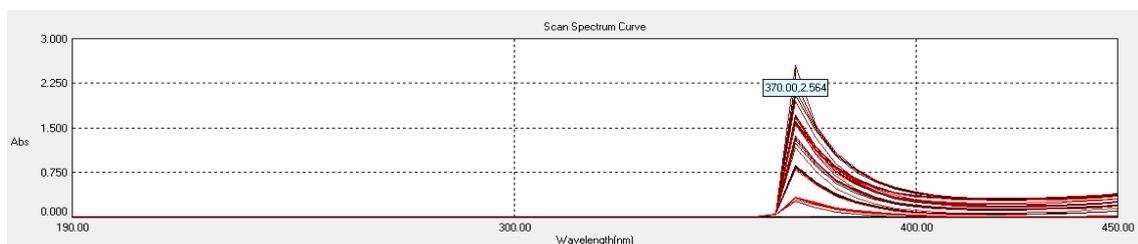


Figure (2)a: two dimensional spectrum for sultam B at 283K, (1:15) molar ratio of (sultam:ICl).

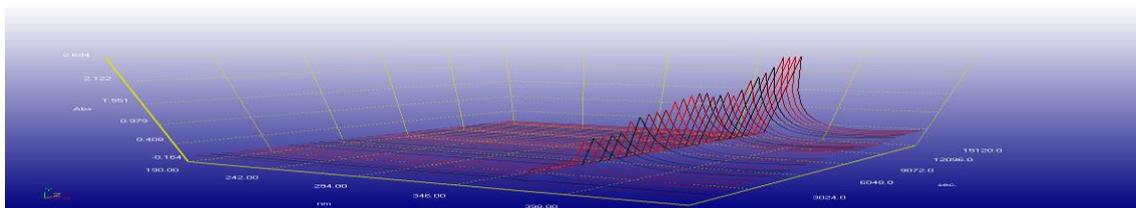


Figure (2)b: three dimensional spectrum for sultam A at 283K, (1:15) molar ratio of (sultam:ICl).

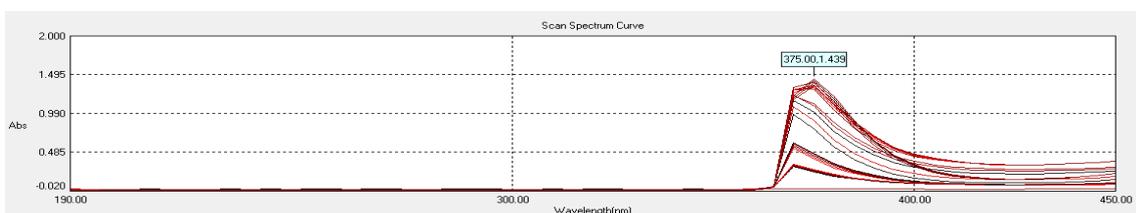


Figure (3)a: two dimensional spectrum for sultam C at 293K, (1:15) molar ratio of (sultam:ICl).

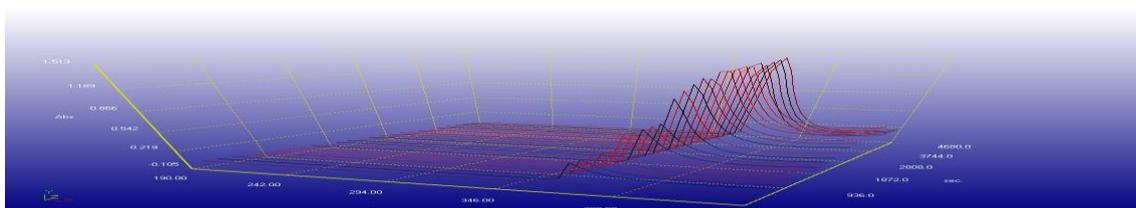


Figure (3)b: three dimensional spectrum for sultam C at 293K, (1:15) molar ratio of (sultam:ICl).

After detecting the λ_{max} ($\lambda_{\text{max}} = 370\text{nm}$) of the product for the reaction, we followed the change of the absorbance of the product with time; as in the fig.(4); the absorbance increase with time, the reaction at 273K needs more time to complete the reaction as compared with other temperatures this is due to that the reaction is normally exponentially dependent on temperature, as the temperature increased the absorbance increased so the rate of reaction increased.

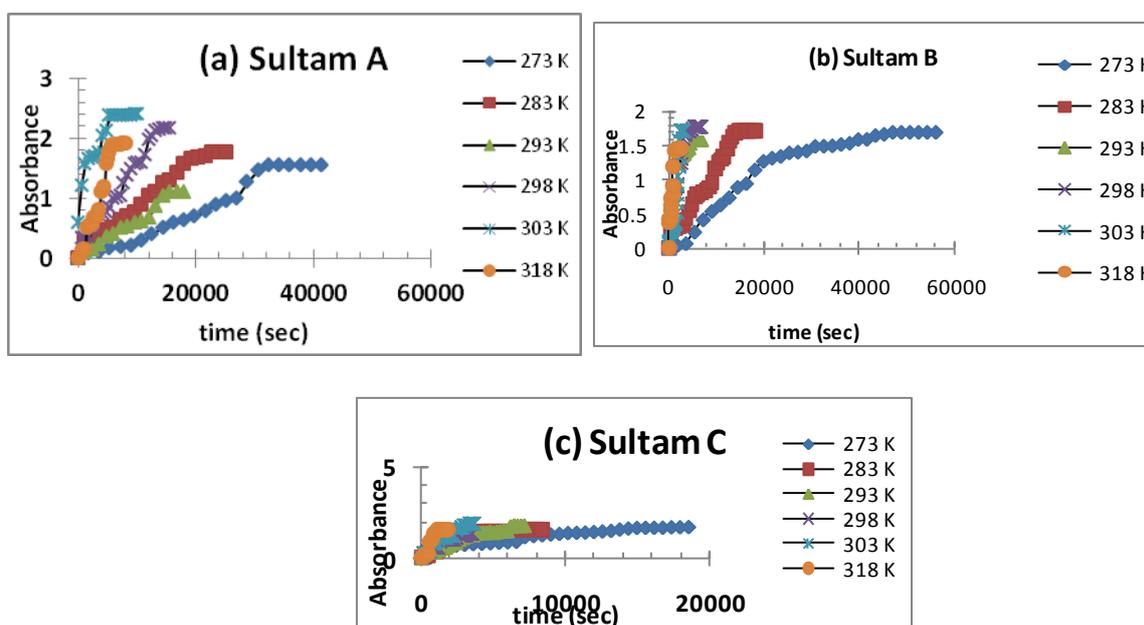


Figure (4): Variation of absorbance of the product with time for iodination of sultams (A, B, C) at different temperature.

The results obtained from the kinetic data for the product of the iodination 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^[14,15]:

$$\ln(A_{\infty} - A_t) = \ln A_{\infty} - k_1 t \quad (1)$$

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 (∞), and also equivalent to the initial concentration of reactant (a). t : time in sec. k_1 : first order rate constant of reaction in sec^{-1} ($A_{\infty}-A_t$): concentration of product at any time, and also equivalent to remaining concentration of reactant (a-x). The value of k_1 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_1 , $t_{1/2}$, 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 $0 \leq R^2 \leq 1$.

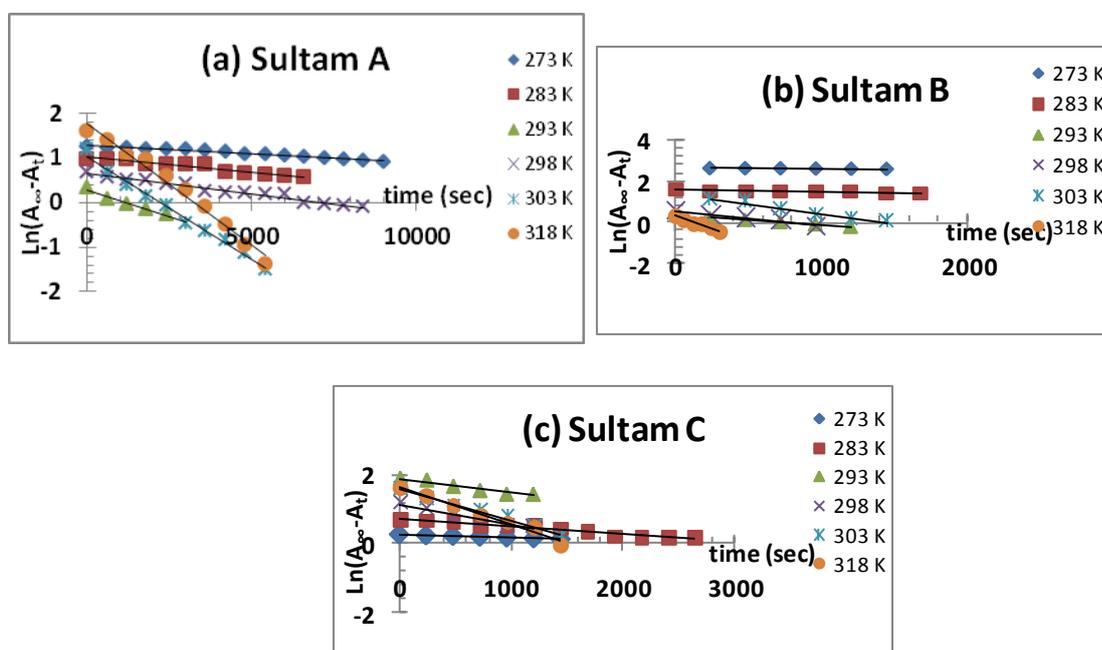


Figure (5): first order plot for the absorbance of the product of sultam (A, B, C) with iodine monochloride in chloroform using 1:15 molar ratio reactants.

Table (2): Observed rate constants, for the iodination of sultams by ICl with molar ratio (1:15).

(a) For sultam A

Temp. (K)	$k_1 \times 10^{-4} (\text{sec}^{-1})$	$t_{1/2}$ (sec)	R^2
273	0.42	16500.0	0.976
283	0.95	7294.7	0.937
293	2	3465.0	0.974
298	2.8	2475.0	0.967
303	4	1732.5	0.990
318	10.6	653.7	0.972

(b) For sultam B

Temp. (K)	$k_1 \times 10^{-4} (\text{sec}^{-1})$	$t_{1/2}$ (sec)	R^2
273	0.16	43312.5	0.928
283	0.45	15400.0	0.948
293	1.19	5823.5	0.998
298	1.87	3705.8	0.936
303	3	2310.0	0.978
318	9	770.0	0.969

(c) For sultam C

Temp. (K)	$k_1 \times 10^4 (\text{sec}^{-1})$	$t_{1/2} (\text{sec})$	R^2
273	0.9	7700.0	0.997
283	2	3465.0	0.958
293	4	1732.5	0.976
298	5	1386.0	0.902
303	7	990.0	0.974
318	16	433.1	0.962

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):

$$\ln k_1 = \ln A - E_a / RT \quad (2)$$

From the obtained results of the activation energy E_a , the enthalpy of activation ΔH^\ddagger , entropy ΔS^\ddagger and Gibbs free energy of activation ΔG^\ddagger can be obtained using equations^[16,17]:

$$\Delta H^\ddagger = E_a - RT \quad (3)$$

$$A = \frac{ek_b T}{h} e^{\frac{\Delta S^\ddagger}{R}} \quad (4)$$

$$\Delta S^\ddagger = R(\ln A - \ln(ek_b T/h)) \quad (5)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (6)$$

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

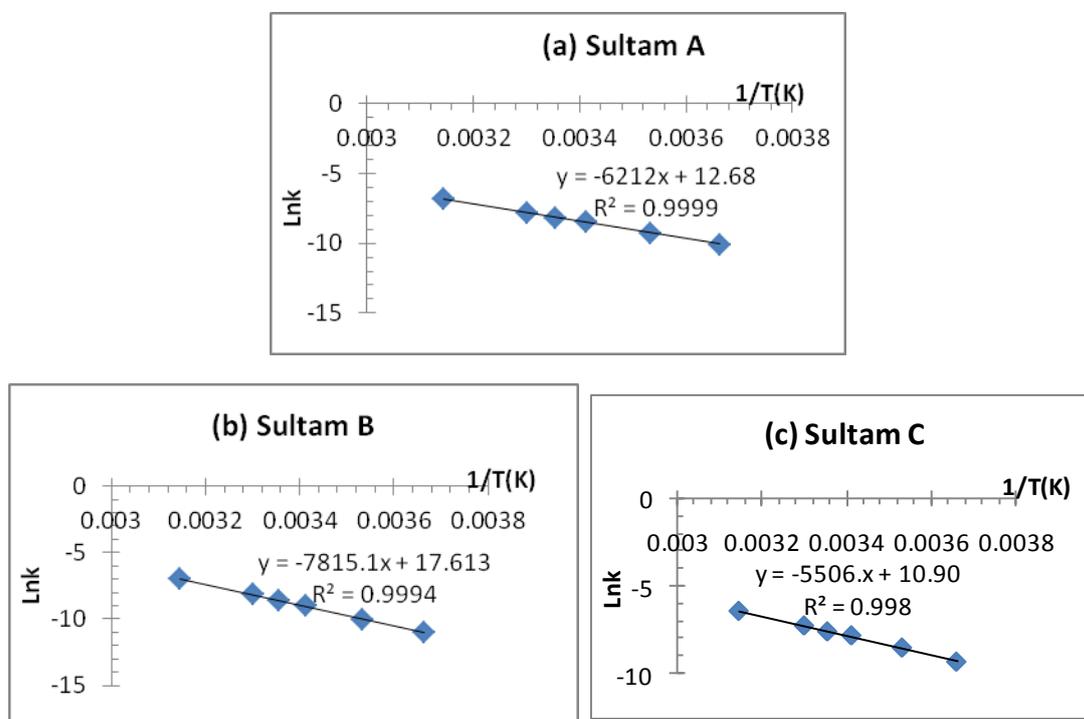


Figure (6): Arrhenius plots for iodination of sultams (A, B, C) at different temperatures using (1:15) molar ratio of sultam: ICl.

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

Sultam	E _a (kJ.mol ⁻¹)	R ²	A-factor/ s ⁻¹	ΔS [#] (J. K ⁻¹ mol ⁻¹) at 298K
A	51.646	0.999	3.212×10 ⁵	-147.798
B	64.974	0.999	4.458×10 ⁷	-106.785
C	45.781	0.998	5.444×10 ⁴	-162.555

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

Sultam	Temp. (K)	ΔH [#] (kJ.mol ⁻¹)	ΔS [#] (J. K ⁻¹ mol ⁻¹)
A	273	49.376	-147.069
	283	49.293	-147.368
	293	49.210	-147.657
	298	49.168	-147.798
	303	49.127	-147.936
	318	49.002	-148.338
B	273	62.705	-106.056
	283	62.621	-106.356
	293	62.538	-106.644
	298	62.497	-106.785
	303	62.455	-106.923
	318	62.330	-107.325
C	273	43.511	-161.827
	283	43.428	-162.126
	293	43.345	-162.415
	298	43.303	-162.555
	303	43.261	-162.694
	318	43.137	-163.095

3.1.2 Interpretation of the overall kinetic and thermodynamic results

Typical plots between $\ln(A_{\infty}-A_t)$ against (t) 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_2 -values calculated in table (2) are very low which means the reactions are very slow and the rate of reaction of studied sultams follows the sequence:



These are depending on the nucleophilicity of the amine (N) group and the substituent on p-position. Table (2) shows the sequence $p\text{-OCH}_3 > \text{H} > p\text{-Cl}$ of the substituent groups, since these groups have different effect on the activating or deactivating of the rate of reactions. This is dependent on the strength of electron-withdrawing or electron-donating groups.

The comparison of the rate constant and the half time of the iodination reaction of unsubstituted sultam(A) with other two different substituted sultams (B and C) at 298K is:

- 1- The unsubstituted sultam (X=H) was taken as a reference reaction rate for comparison ($k_2=2.8 \times 10^{-4} \text{ sec}^{-1}$) ($t_{1/2} = 2475 \text{ sec.}$).
- 2- When (X= p-Cl) which is electron withdrawing group, it reduces electron density at the reaction center. As a result the rate of reaction decreased ($k_2=1.87 \times 10^{-4} \text{ sec}^{-1}$), i.e. $t_{1/2}$ increased ($t_{1/2} = 3705.8 \text{ sec.}$).
- 3- When (X= p-OCH₃) which is electron donating group, thus enrich electron density at the reaction center of the formed activated complex. The rate of reaction increased ($k_2=5 \times 10^{-4} \text{ sec}^{-1}$), i.e. $t_{1/2}$ decreased ($t_{1/2} = 1386 \text{ sec.}$).

We investigated the activation parameters for iodine attack to sultam in chloroform solution, and the results are visualized in fig.(6) and in tables(3) and (4). The highest activation energy ($E_a = 64.974 \text{ kJmol}^{-1}$) for the iodination of sultam B explains the slowness of the reaction, which means that the reactants need high energy for transition state, this is due to the electron withdrawing group (p-Cl) substituent, while E_a value was smaller for sultam C ($E_a = 45.781 \text{ kJmol}^{-1}$) that means easier reaction will occur. The values of ΔH^\ddagger are positive means consumes energy in its process. Relatively low values of (A) pre-exponential factor for sultam C were explained according to the transition state theory^[18], 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):

$$A = \frac{k_b T}{h} * \frac{Q_{AB}^*}{Q_A Q_B} \quad (7)$$

Which indicate the more rigid configuration with less degree of freedom for the activated complex which has a simpler configuration than the reactant molecules. The study of the iodination of sultams are gave negative low values for ΔS^\ddagger as shown in table (4), which indicates the more rigid configuration with less degree of freedom for the activated complex than those of the reactant molecules.

- 1- ΔS^\ddagger for the reaction between ICl and unsubstituted sultam (X=H) equal to $-147.798 \text{ JK}^{-1}\text{mol}^{-1}$ is considered as a reference for comparison with the substituted sultam.
- 2- (X = p-Cl) the presence of electron withdrawing group lead to higher negative value of $\Delta S^\ddagger = -106.785 \text{ JK}^{-1}\text{mol}^{-1}$, leads to a less aligned and unstable transition state.
- 3- Low negative value of $\Delta S^\ddagger = -162.555 \text{ J K}^{-1}\text{mol}^{-1}$ for (X= p-OCH₃) for electron donating groups, which cause increasing electron density at the reaction center which allow for relatively better attack of the ICl to obtained a more stable transition state.

3.2 The iodination using sultam : ICl (15:1) molar ratio

Sultam:ICl (15:1) the physical properties, H^1 - and C^{13} -nmr, IR and Uv-data are all very close to that of the unsubstituted (by iodine) sultams. Of course a reaction has been achieved between 1mmole of ICl and 15mmole sultam but the product disappeared between the large quantities of sultam, in addition to that the product is more soluble in solvents than sultam itself during recrystallization and this is one of the reason that the product is undetectable even by IR, H^1 -nmr and C^{13} -nmr and so it wasn't possible to do kinetic work for these reactions.

3.3 The iodination using sultam : ICl (1:1) molar ratio

The study of iodination of sultams also carried out using equi molar ratio of each reactants (sultam and ICl), the two and three dimensional absorption spectra, fig.(7)to(9), are represents the results of kinetic measurements for three sultams at six different temperatures (between 273-318K), and the variation of absorbance of the peaks with time are shown in fig.(10) as we see the absorbance of the product increase with time indicating that the reactions are clean forward processes, since no equilibrium was observed during kinetic runs.

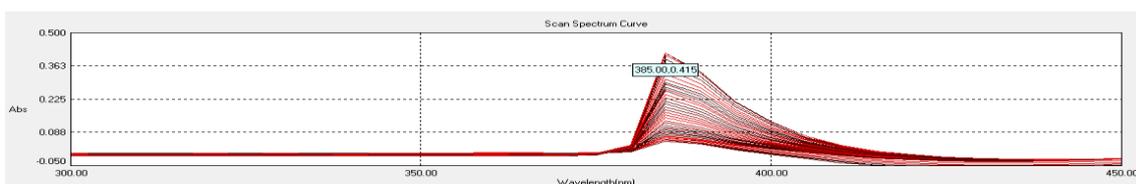


Figure (7)a: two dimensional spectrum for sultam A at 303K, (1:1) molar ratio of (sultam:ICl).

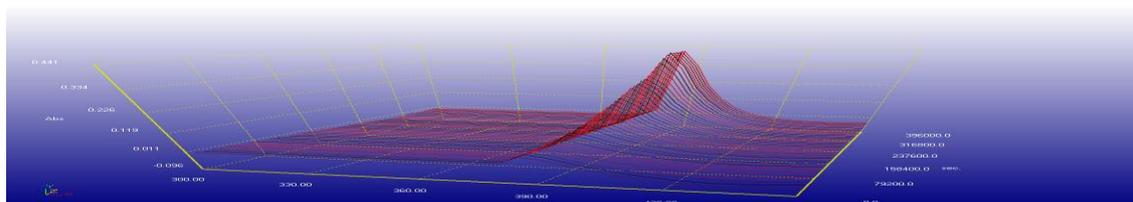


Figure (7)b: three dimensional spectrum for sultam A at 303K, (1:1) molar ratio of (sultam:ICl).

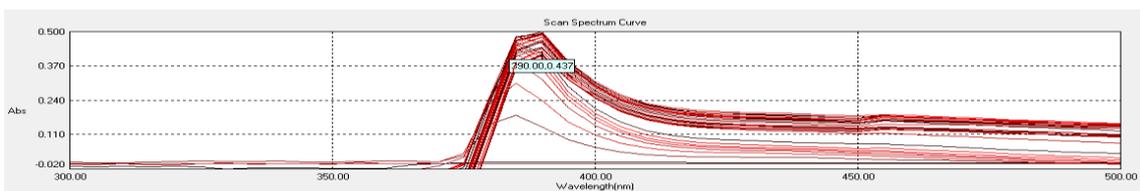


Figure (8)a: two dimensional spectrum for sultam B at 293K, (1:1) molar ratio of (sultam:ICl).

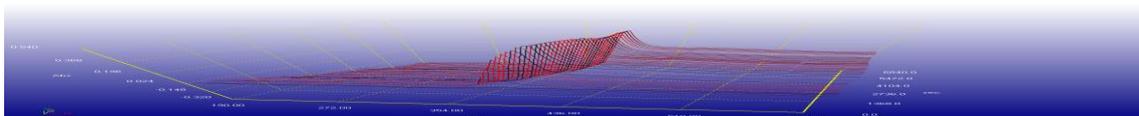


Figure (8)b: three dimensional spectrum for sultam B at 293K, (1:1) molar ratio of (sultam:ICl).

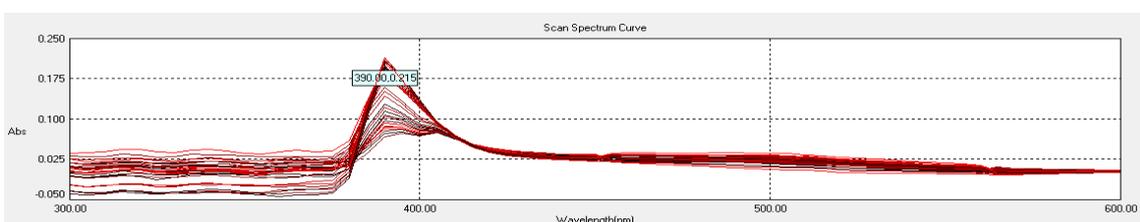


Figure (9)a: two dimensional spectrum for sultam C at 283K, (1:1) molar ratio of (sultam:ICl).

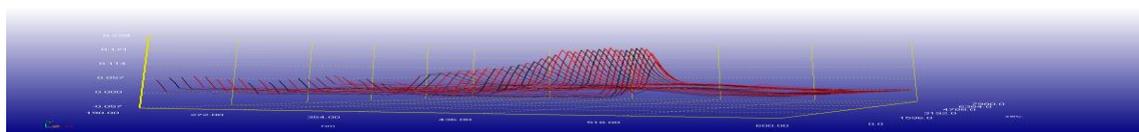


Figure (9)b: three dimensional spectrum for sultam C at 283K, (1:1) molar ratio of (sultam:ICl).

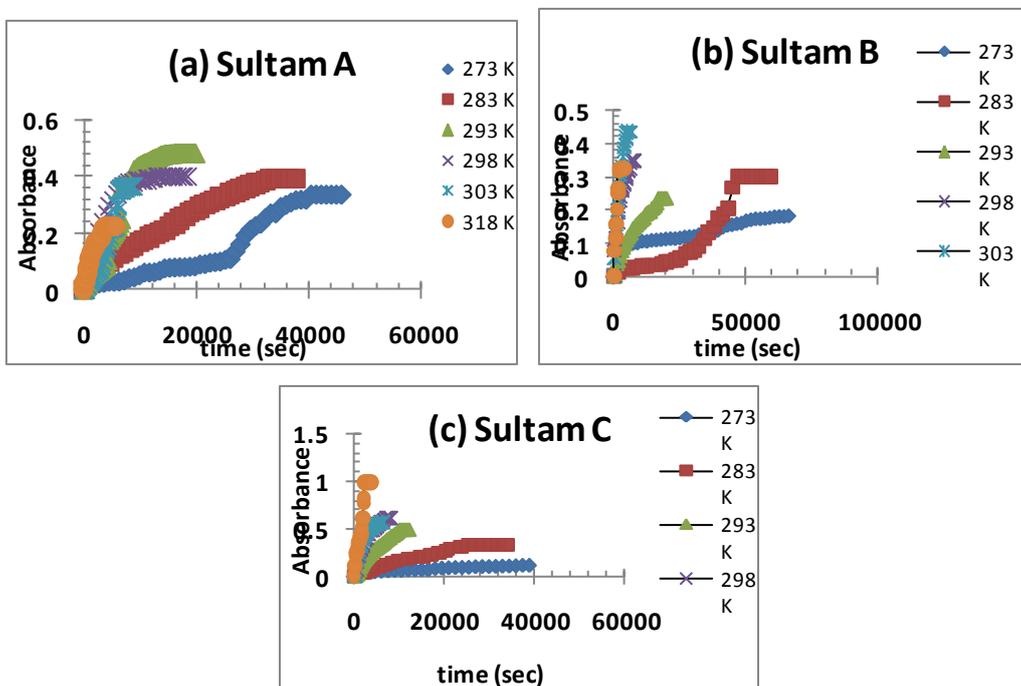


Figure (10): Variation of absorbance of the product with time for iodination of sultams (A, B, C) at different temperatures using (1:1) molar ratio of sultam: ICl.

The rate law can be expressed by the equation:

$$\frac{d[\text{product}]}{dt} = k_2[\text{ICl}][\text{Sultam}] \quad (8)$$

These reactions were determined as second order equation; first-order with respect to each reactant and can be described by equation (9)^[19-22]:

$$\frac{A_t}{A_\infty(A_\infty - A_t)} = k_2 t \quad (9)$$

Which means that the straight line plot of $A_t/(A_\infty(A_\infty - A_t))$ with the time (t) has a slope (k_2) 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 and c).

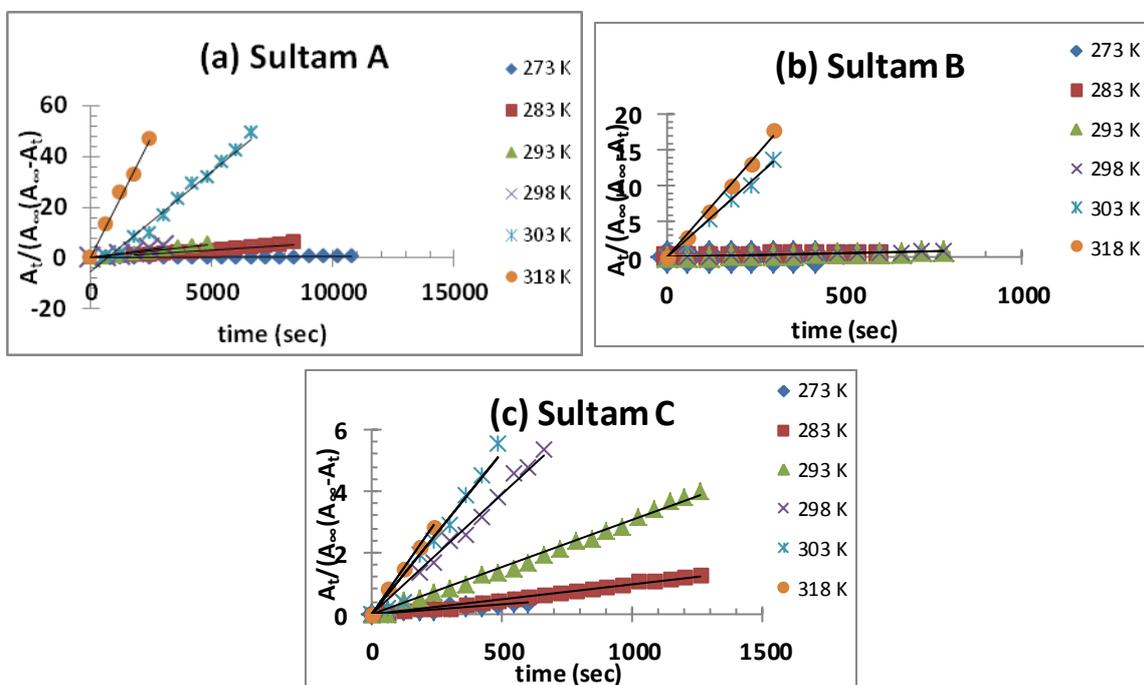


Figure (11): Second order plot for the absorbance of the product for iodination of sultams (A, B, C) at different temperatures using (1:1) molar ratio of sultam:ICl.

Table (5): Observed rate constants, for the iodination of sultams A with ICl with (1:1) molar ratio.

(a) For sultam A

Temp. (K)	$k_2 \times 10^{-4} \text{ (sec}^{-1} \cdot \text{dm}^3 \cdot \text{mol}^{-1}\text{)}$	$t_{1/2} \text{ (sec)}$	R^2
273	2.9	34690.9	0.980
283	7.8	12897.9	0.952
293	19	5294.9	0.972
298	31	3245.2	0.948
303	70	1437.1	0.930
318	190	529.4	0.914

(b) For sultam B

Temp. (K)	$k_{\text{obs}} \times 10^{-4} \text{ (sec}^{-1} \cdot \text{dm}^3 \cdot \text{mol}^{-1}\text{)}$	$t_{1/2} \text{ (sec)}$	R^2
273	2	50301.8	0.944
283	8	12575.4	0.966
293	13	7738.7	0.991
298	29	3469.0	0.981
303	69	1458.0	0.955
318	185	543.8	0.905

(b) For sultam C

Temp. (K)	$k_{\text{obs}} \times 10^4$ ($\text{sec}^{-1} \cdot \text{dm}^3 \cdot \text{mol}^{-1}$)	$t_{1/2}$ (sec)	R^2
273	6	16767.2	0.980
283	14	7185.9	0.992
293	34	2958.9	0.943
298	51	1972.6	0.905
303	72	1397.2	0.945
318	129	779.8	0.984

3.3.1 Interpretation of the overall kinetic and thermodynamic results

Applying pseudo second order equation and plotting $A_t/(A_\infty(A_\infty - A_t))$ with time (sec) produces a straight line as in fig. (11), the k_2 value obtained for sultam (B) ($k_2 = 29 \times 10^{-4} \text{sec}^{-1} \text{dm}^3 \text{mol}^{-1}$) at 298K was smaller than for sultam (A) ($k_2 = 31 \times 10^{-4} \text{sec}^{-1} \text{dm}^3 \text{mol}^{-1}$) at 298K, this is due to the electron withdrawing effect of the chlorine which deactivate the reaction center, But when (X=p-OCH₃) in sultam (C) which is electron donating group, which activate the reaction center and the rate of reaction increased ($k_2 = 51 \times 10^{-4} \text{sec}^{-1} \text{dm}^3 \text{mol}^{-1}$) and the obtained kinetic data are summarized in table (5) for which R^2 value indicates a very good fitness. Results of table (5) indicate slower reaction rate of iodine monochloride with sultam B than with sultam A and faster for sultam C, due to electronic (withdrawing or donating) groups on the phenyl ring of the sultam that effects on the electrophilic substitution reaction.

From Arrhenius plots for iodination of sultams (A, B and C) at six different temperature ranged (273-318K) (fig.(12)) E_a and A-values are obtained, E_a value for sultam (B) has higher value because p-substituted chlorine is electron withdrawing group which decrease the electrophilicity of sultam to attack the iodine monochloride for electrophilic aromatic substitution. While sultam (C) has smaller E_a value due to (p-OCH₃) electron donating group which increase the electrophilicity of the sultam.

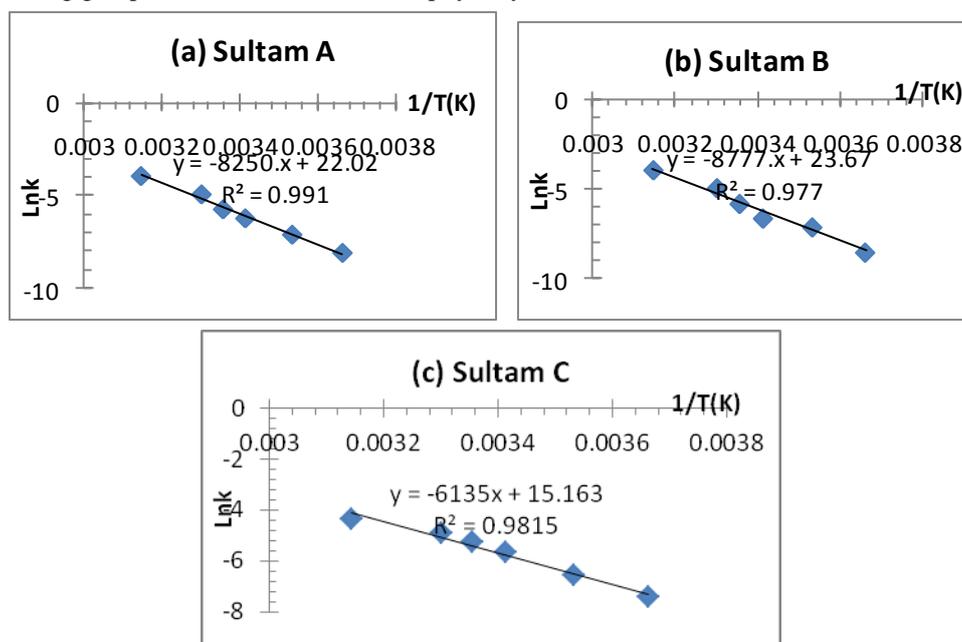


Figure (12): Arrhenius plots for iodination of sultams (A, B, C) at different temperatures using (1:1) molar ratio of sultam: ICl.

The analogous interpretation of the A-factor is that it is a measure of the rate at which collisions occurred irrespective of their energy. Hence the product of A-factor gives the rate of successful collisions^[22]. The entropy of activation gives a measure of the inherent probability of the transition state, apart from energetic considerations, if ΔS^\ddagger is large and negative, the formation of the transition state requires the reacting molecules to adopt precise conformations and approach one another at a precise angle. As molecules vary widely in their conformational stability, in their rigidity, and in their complexity, one might expect the values of ΔS^\ddagger to vary widely between different reactions^[22].

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

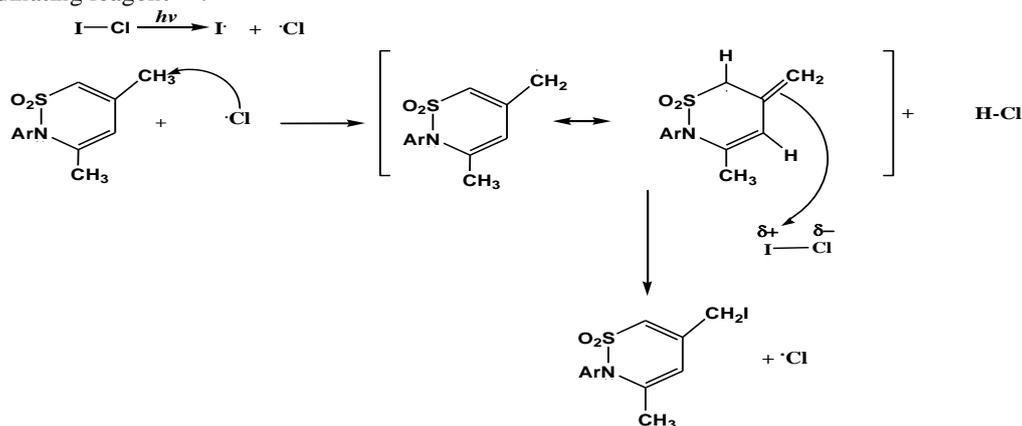
Sultam	E_a (kJ.mol ⁻¹)	R^2	A-factor (s ⁻¹ .dm ³ .mol ⁻¹)	ΔS^\ddagger (J. K ⁻¹ mol ⁻¹) at 298K
A	68.592	0.991	3.657×10^9	-70.145
B	72.977	0.978	1.914×10^{10}	-56.385
C	51.006	0.981	3.847×10^6	-127.154

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

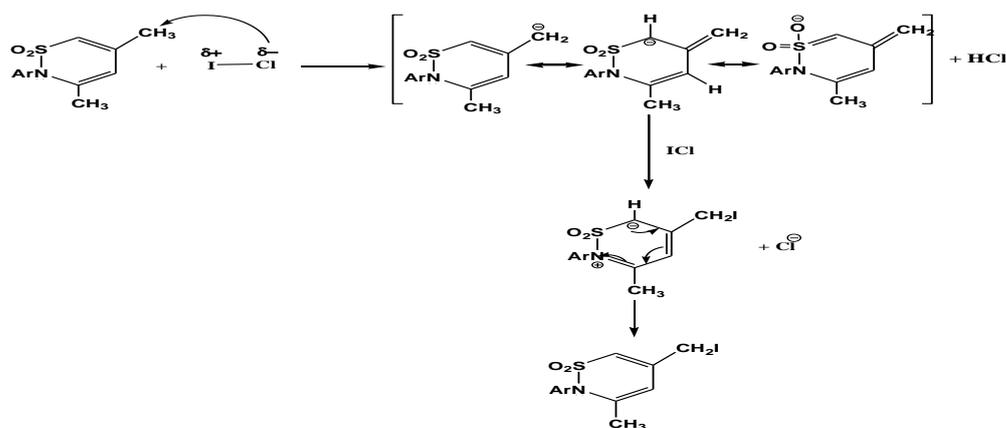
Sultam	Temp. (K)	ΔH^\ddagger (kJ.mol ⁻¹)	ΔS^\ddagger (J. K ⁻¹ mol ⁻¹)
A	273	66.322	-69.417
	283	66.239	-69.716
	293	66.156	-70.004
	298	66.114	-70.145
	303	66.073	-70.283
	318	65.948	-70.685
B	273	70.707	-55.657
	283	70.624	-55.956
	293	70.540	-56.245
	298	70.499	-56.385
	303	70.457	-56.524
	318	70.333	-56.925
C	273	48.736	-126.426
	283	48.653	-126.725
	293	48.570	-127.014
	298	48.528	-127.154
	303	48.487	-127.293
	318	48.362	-127.694

3.4 Reaction mechanism

It is seldom, if ever, possible to provide complete and entire information, structural, energetic, and stereochemical, about the pathway that is traversed by any chemical reaction: no reaction mechanism can ever be proved to be correct. Based on the results obtained we propose a mechanistic explanation illustrated in scheme (2) and (3) to account for the products formed, but the most preferable and accepted mechanism is scheme(3) Due to the electronegativity difference between chlorine and iodine, ICl is highly polar and behaves as an iodinating reagent^[23].



Scheme (2)



Scheme (3)

IV. 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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