Kinetic Characteristics for Reaction between Trichloroisocyanuric (TCCA) Acid with 2-Chlorobenzylidene Malononitrile (CS)

Chu Thanh Phong[1], Vo Thanh Vinh[2], Nguyen Khanh Hung[3], Tran Van Chung[4]

[1]Institute of New Technology, 17 Hoang Sam street, Cau Giay district, Hanoi, Vietnam
[2,3] Centre for Technology Environmental Treatment, 17 Hoang Sam street, Cau Giay district, Hanoi, Vietnam
[4]Institute of Chemicals and Material. 17 Hoang Sam street, Cau Giay district, Hanoi, Vietnam

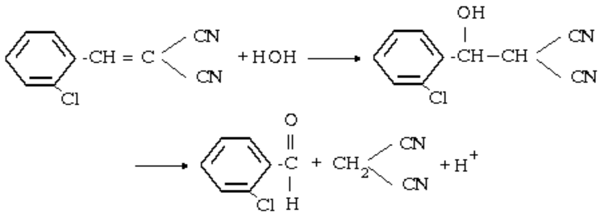
***Abstract*—** *The research experimental results determiningrateconstant of the reaction between TCCA and CS according to Arrhenius equation was studied. Basing the set of graphs showing the relationship between (ln(k) - (1/T)) and (ln (k/T) - (1/T)), the activation energy (E_a) according to the Arrhenius equation and activation enthalpy variation ($\Delta H^\#$), activationentropy variation ($\Delta S^\#$), free activation energy Gibss ($\Delta G^\#$) according to the Eyring equation are determined. The products of TCCA reaction and CS at pH = 9 are2-chloro benzaldehyde oxirane-2,2-dicarbonitrile, 3-(2-chlorophenyl) so predicting the reaction mechanism consists of two reactions taking place in parallel, a hydrolysisand oxidation reactions.*

Keywords*— *Trichloroisocyanuric acid, 2-chlorobenzylidene malononitrile, Kinetic characteristics.

I. INTRODUCTION

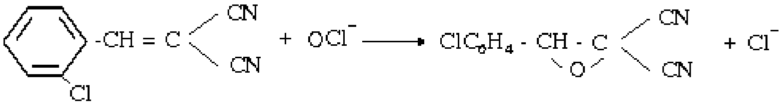
2-chlorobenzylidene malononitrile (CS) is heavily used in the Vietnam War, statistics show that about 9,000 tons of CS were used on the battlefield [1]. Due to being durable, difficult to decompose, it can be found that CS existed since the war in Central and Southern Vietnam. That the reason we need to deal with the amount of residual CS found. Reactions that are often used to dissolve CS [4], [8] include:

CS hydrolysis reaction takes place as follows:



(1)

and CS oxidation reaction by OCl- takes place as follows:



(2)

Acid trichloroisocyanuric (TCCA) is hydrolyzed to form hypochlorous acid HOCl and acid cyanuric as following [3]

$C_3N_3O_3Cl_3 + 3H_2O \leftrightarrow C_3N_3O_3H_3 + 3HOCl$

However, not all chlorine content in TCCA hydrolyzed into HOCl. Thus a part of chlorine still exists in TCCA called bound available chlorine [6]. TCCA is hydrolyzed to produce HOCl and depending on pH and then HOCl proceeding hydrolyze to form OCl^- [7].

$$HOCl \leftrightarrow OCl^- + H^+ \quad (3)$$

So, the solution TCCA has a pH> 7 that can react with CS in two reactions (1) and (2). From the Arrhenius equation, E_a - activation energy (kJ/mol) was determined [6]; From the Eyring equation determine $\Delta H^\#$ - Activated enthalpy variation (kJ/mol), $\Delta S^\#$ - Activated entropic variation (kJ/mol.K) and calculate $\Delta G^\#$ - Free energy variability Activated Gibbs (kJ/mol) [6]. Use GC/MS method to determine the product of TCCA reaction and CS from which to predict the mechanism of reaction.

II. EXPERIMENTAL

2.1 Apparatus and Chemicals

2.1.1 Apparatus

UV-Vis Spectrophotometer UV-VIsJasco V530, Japan

Gas chromatography/Mass spectrometry GC 6895 / MS HP 5975A, USA

2.1.2 Chemicals

TCCA (Sigma - Aldrich);

Solid CS with 99.0% purity (Vietnam);

Other used chemicals for research and analysis include: Na_2SO_4, phosphate buffer pH = 9, NaOH, KCl, H_2SO_4, $FeCl_2$, sodium 1,2-naphthoquinone-4-sulfonate, ethanol, (Pa, Sigma- Aldrich) , acetonitrile, methanol, dichloromethane, cloroform, n-hexane (Pa, Merck).

2.2 Experimental procedure

2.2.1 Prepare the solution

Mix 50 mg of CS in 100 ml of ethanol to obtain CS solution with a concentration of 495.00 mg / L (2.652 mM / L) to obtain solution S1.

Mixing 960 mg of TCCA in 500ml of distilled water obtained TCCA solution with a concentration of 1,920.00 mg / L (8.261 mM / L) obtained S2 solution.

Take in the reaction flask 5ml of phosphate buffer pH = 9, 10mL of solution S1, 10mL of solution S2 to obtain solution S3 have: C_{CS} = 198.00 mg / L; C_{TCCA} = 768.01 mg / L.

2.2.2 Determine the parameters of the reaction

2.2.2.1 Determine the reaction level

After 3-minute; 5 minutes; 10 minutes; 15 minutes; 25 minutes, take sample S3 solution, analyze the remaining CS concentration. Develop a graph showing the relationship ($\ln(C_{CS}) = f(t)$). If the graph is linear, then the reaction is an apparent pseudo first order reaction.

2.2.2.2 Determine the reaction rate constant

Determine the reaction rate constant. If the reaction between TCCA and CS determined according to 2.2.2.1 is level 1, the reaction rateis expressed by the equation:

$$v = \frac{-dC}{dt} = k_A(C_o - x) \tag{4}$$

In which: k_A is the reaction rate constant according to Arrhenius (s^{-1})

C_o is the concentration of CS at time t = 0 s (mol/L)

x is the concentration of CS participated in the reaction

$$(C_o - x) = C_{CS}$$

In which: C_{CS} is the concentration of CS at time t in solution (mol/L)

Transformation (4) is obtained:

$$\ln(C_{cs}) = - k_A t + CT \tag{5}$$

In which: CT is an integral constant

t is the reaction time (s)

The equation has the form of $y = ax + b$ with $y = \ln(C_{cs})$; $a = - k_A$; $x = t$; $b = CT$.

The reaction rate constant is determined as follows:

$$k_A = - a \tag{6}$$

2.2.2.3. Determination of E_a according to the Arrhenius equation

Arrhenius equation is as follows:

$$k_A = Ae^{\frac{-Ea}{RT}} \tag{7}$$

Inside:

k_A is the reaction rate constant according to Arrhenius (s^{-1})

T is the absolute temperature (K)

A is the exponential factor. According to collision theory, A depends on the frequency of collisions in the right direction and is considered to be independent of T.

E_a is activation energy (kJ/mol)

R is the ideal gas constant (R = 8,315 J/mol.K)

The transformation of equation (7) is obtained:

$$lnk_A = \frac{-E_a}{RT} + lnA \tag{8}$$

Equation (8) has the form of y = ax + b with y = ln (k_A); a = - E_a/R; x = 1 / T; b = lnA.

Maintain the temperature of S3 solution at the temperature respectively: 293 K, 298 K, 303 K, 313 K. Determine the reaction rate constant at the temperatures according to 2.2.2.2.

Develop a graph showing the relationship (ln($k_{A\text{-}CS}$) = f(1/T)). Then, activation energy is calculated according to the formula:

$$E_a = - a.R \text{ (J/mol)} \tag{9}$$

2.2.2.3. Determinination of $\Delta H^\#$, $\Delta S^\#$, $\Delta G^\#$ according to the Eyring equation:

Eyring equation:

$$k_A = \frac{k_B T}{h} e^{\frac{-\Delta H^\#}{RT}} e^{\frac{\Delta S^\#}{R}} \tag{10}$$

Equation transformation (10):

$$ln\frac{k_A}{T} = -\frac{\Delta H^\#}{R}\frac{1}{T} + ln\frac{k_B}{h} + \frac{\Delta S^\#}{R} \tag{11}$$

Equation (11) has the form of y = -ax + b, where x = 1/T; y = ln (k_A/T); and $a = \frac{-\Delta H^*}{R}$, $b = ln\frac{k_B}{h} + \frac{\Delta S^*}{R}$

From that set of graphs shows the relationship between (ln(k) - (1/T)) (11):

$$\Delta H^\# = -a.R \text{ (J/mol)} \tag{12}$$

$$\Delta S^\# = R(b - ln(k_B/h) \text{ (J/mol.K)} \tag{13}$$

Free activation energy Gibss ($\Delta G^\#$) follows the equation:

$$\Delta G^\# = \Delta H^\# - T\Delta S^\# \text{(J/mol)} \tag{14}$$

2.2.3. Methods of analysis

2.2.3.1. Analysis of CS by UV-Vis Spectrophotometry

Sampling S3 solution in experiments, analyzing CS concentration on the Jasco-V530 UV / VIS device based on the reaction between CS and 1.2 naphtoquynon-4-sunfonatnium reagent in alkaline medium, CS concentration in The solution is determined by measuring the optical absorbance of the solution and comparing it with the calibration graph. Analytical samples were dissolved in solvents; dehydration in the analytical sample by Na_2SO_4; Filter about 5 µl as a sample by Whatman filter [2].

2.2.3.2. Analysis of reaction products by GC/MS

Sampling solution S3 when t = 25 minutes, T = 298 K, product analysis of the reaction between TCCA and CS on HP 5975A device. Sample run program [5]: Using 03 column types with different degree of polarization are: SPB1 column size (30m*0.32mm*0.25µm); DB5-MS column size (30m*0.32mm*0.25µm), column OV1701 size (30m*0.32mm*0.25µm). Temperature at the beginning of column 60^0C, hold for 1 minute, increase 8^0C/min to 280^0C, keep at that temperature for 10 minutes. Air flow rate carries (He) is 1mL/min. Scan range of 45-800M/z. Universal library NIST 2005 with about 195.000 substances.

III. RESULT AND DISCUSSION

3.1 Level of reaction between TCCA and CS

The graph shows the relationship ($\ln(C_{CS})$-t) of CS reaction with TCCA at 298 K shown in Figure 1.

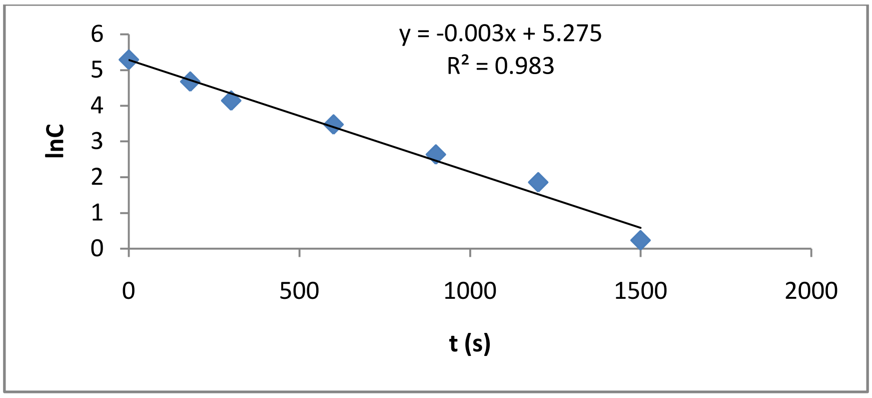


FIGURE 1. Graph of relationship representation ($\ln(C_{CS})$-t) of CS response with TCCA

From Figure 1, the reaction between TCCA and CS has C_{CS} concentration decreased linearly over time (t), so the reaction between CS and TCCA is pseudo first order reaction with a correlation coefficient R^2 = 0.9832.

3.2 Kinetic study of TCCA reaction with CS

Rate constant of reaction between TCCA and CS at different temperatures in Table 1.

TABLE 1
THE REACTION RATE CONSTANT BETWEEN TCCA AND CS AND CORRELATION COEFFICIENTS AT DIFFERENT TEMPERATURES

Number order	Kind	k (s^{-1})	R^2
1	TCCA-CS-293	0.0014	0.9680
2	TCCA-CS-298	0.0031	0.9832
3	TCCA-CS-308	0.0043	0.8845
4	TCCA-CS-318	0.0069	0.9306

From Table 1, the reaction rate constant in TCCA-CS systems increases with increasing temperature, consistent with the Arrhenius equation. The correlation coefficients of the graph represent each middle relationship ($\ln(C_{CS})$-t) at different temperatures ranging from 88.45% (TCCA-CS-308) to 98.32% (TCCA-CS-293).

Based on the value of the reaction rate constant in Table 1, plot the representation of each relationship between ($\ln(k_{CS})$-(1/T)) and ($\ln(k_{CS}/T)$-(1/T)). The results are shown in Figure 2.

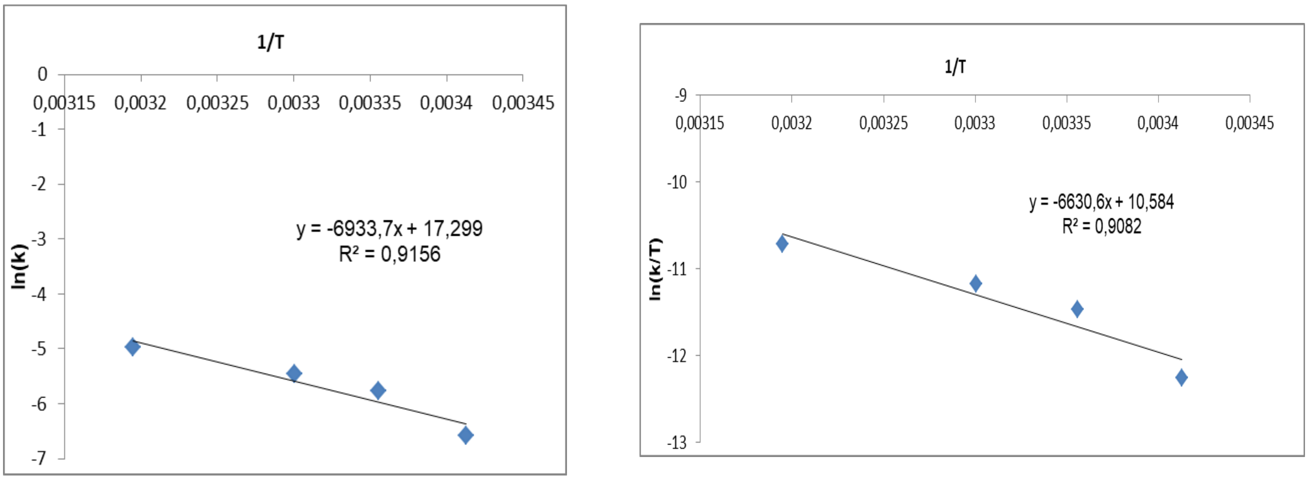


FIGURE 2. The graph shows each relationship between (a) ($\ln(k_{CS})$-(1/T)) and (b) ($\ln(k_{CS}/T)$-(1/T)) in the TCCA-CS

From Figure 2, determine the E_a value according to (9) and ΔH#, ΔS#, ΔG# according to (12), (13), (14) as shown in Table 2.

TABLE 2
THERMODYNAMIC PARAMETERS OF TCCA REACTION WITH CS

Parameter	Value	R^2
E_a (kJ/mol)	57.65	0.9156
lnA	17.299	0.9156
$\Delta H^{\#}_{298}$ (kJ/mol)	55.13	0.9082
$\Delta S^{\#}_{298}$ (kJ/mol.K)	-0.11	
$\Delta G^{\#}_{298}$ (kJ/mol)	87.78	

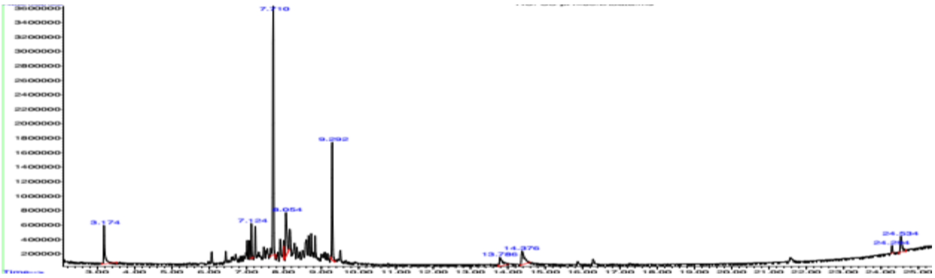
From Table 2, we see:

- E_a value of TCCA reaction with CS is consistent with experimental data in the range of 20 - 150 kJ/mol.
- Positive $\Delta H^{\#}_{298}$ values indicate that the reaction to form the active complex is the heat recovery reaction. At the same time, the value of $\Delta H^{\#}_{298}$ is also smaller than Ea in accordance with activated theory and activated complex theory.
- The value of $\Delta S^{\#}_{298}$ negative indicates that the number of particles in the system reduced means the formation of active complexes, in accordance with the active complex theory.
- Value $\Delta G^{\#}_{298}$ positive shows the process of needing energy to form an activated complex.

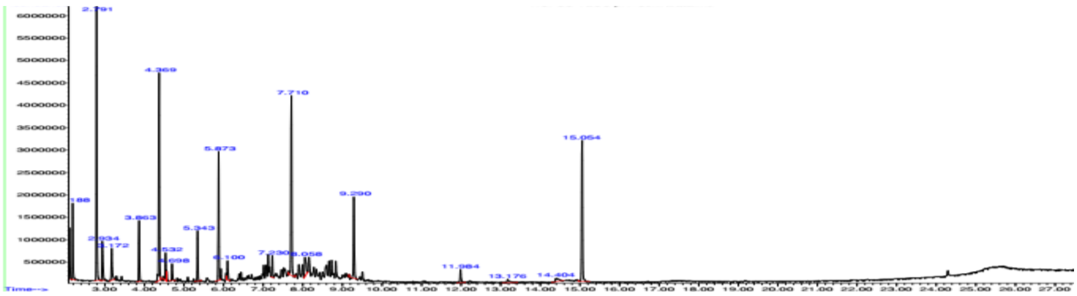
This is consistent with the enthalpy variation of the system.

3.3 Determine the product of the reaction between TCCA and CS

GC/MS chromatogram of post-reaction solution of TCCA-CS system in Figure 3.



(a)



(b)

FIGURE 3. GC chromatography of (a) CS solution at pH = 9 and (b) reaction product of TCCA-CS

According to the chromatogram of the reaction product of TCCA-CS system (Figure 3. a) and the NIST spectrum of MS-library 2005, there was no pic with the time of retention in the reaction solution. It was t_R = 14.367 minutes for 2-Chlorobenzalmalononitrile (CS). This proves that there is no CS in the post-reaction solution.

On the chromatogram of the reaction product solution (Figure 3. b), there appears pic with retention time of t^1_R = 8.154 minutes corresponding to 2-chloro benzaldehyde and pic has a retention time of t^2_R = 12.2 minutes corresponding to oxirane-2, 2-dicarbonitrile, 3- (2-chlorophenyl).

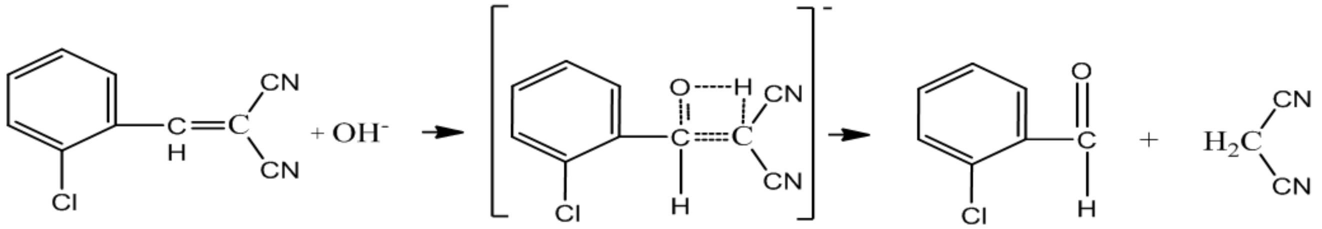
From the theory of CS poisoning and the results of product analysis of the toxic reaction CS by TCCA, can be predicted at pH = 9 TCCA with hydrolysis and the poisoning process consists of two reactions that occur in parallel and create products as follows:

TCCA hydrolysis reaction:

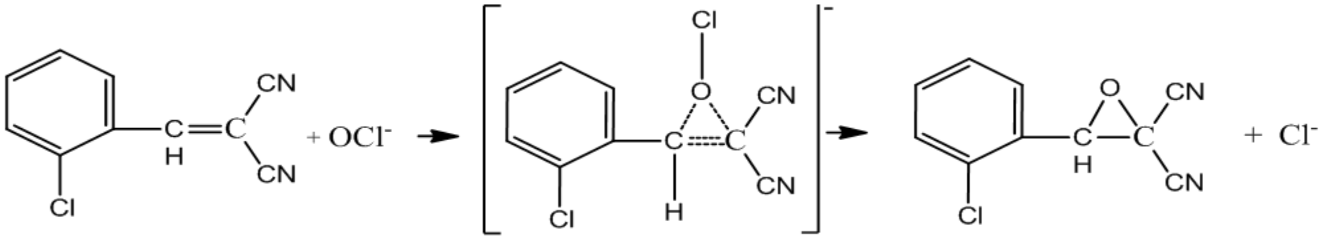
$$C_3N_3O_3Cl_3 + 3H_2O \leftrightarrow C_3N_3O_3H_3 + 3HOCl$$

$$HOCl \leftrightarrow OCl^- + H^+$$

Hydrolysis reaction:



Redox reaction:



IV. CONCLUSION

From the results of the study it can draw the following conclusions:

- The reaction between TCCA and CS is consistent with collision theory and activated complex theory.
- The reaction between TCCA and CS at 298 K is a pseudo- first-order reaction with k_A = 0.0031 (s^{-1}), E_a = 57.65 (kJ/mol); $\Delta H^{\#}_{298}$ = 55.13 (kJ/mol); $\Delta S^{\#}_{298}$ = -0.11 (kJ/mol.K); $\Delta G^{\#}_{298}$ = 87.78 (kJ/mol).
- The reaction between TCCA and CS includes two parallel reactions that are hydrolysis reaction and oxidation reaction, producing two main products such as 2-chloro benzaldehyde and oxirane-2,2-dicarbonitrile, 3- (2 -chlorophenyl).

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