Study of Xanthate Decomposition in Aqueous Solutions

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Abstract

Xanthate is one of the commonly used collectors in froth flotation beneficiation of sulfide ores. It ~~could~~ decomposes and generates toxic compounds such as carbon disulfide (CS₂) which is a concern in the mining industry. A vast body of literature exists for studies on xanthate/mineral interactions, but xanthate decomposition under various conditions (e.g., in solutions or flotation pulps) is not fully understood. We have undertaken detailed studies to fill this knowledge gap, and this paper shows our study of the xanthate decomposition in aqueous solutions in the absence of minerals. This condition has not been appropriately examined by past researchers, while decomposition under this condition is used as control to other complicated ones (e.g., in flotation pulps). A GC-MS based method was developed to directly measure the decomposition products in the gas phase. Decomposition kinetics was then established based on the generation of CS₂. Decomposition followed the first order kinetics, and the rate constant for Sodium *iso*-Butyl Xanthate (SIBX) at neutral pH level was determined to be $9.3 \times 10^{-4} \text{ h}^{-1}$ at 25 °C, $1.7 \times 10^{-2} \text{ h}^{-1}$ at 50 °C and $1.3 \times 10^{-1} \text{ h}^{-1}$ at 70 °C. The effect of pH on decomposition behavior was examined in the pH range of 1.5 to 12.5. We determined experimentally a maximum in the extent of decomposition ~~extent~~ as a function of pH, which was predicted theoretically in literature. A mechanism involving multiple reactions that occurred in parallel or ~~in sequence~~ sequentially along with the decomposition was proposed to explain the observed change of xanthate decomposition ~~in over~~ the entire pH range. These results offer valuable insights and can serve as the basis to mitigate the detrimental effects of xanthate decomposition in plant

operations, for example, by modifying plant parameters to reduce xanthate decomposition without sacrificing its performance.

Key Words:

Xanthate, Decomposition in Aqueous Solutions, Decomposition Rate, Carbon Disulfide

Introduction

Xanthate (or alkyl dithiocarbonate, $R-OCS_2^-$) is a widely used collector in the flotation beneficiation of base metal (such as copper, nickel, zinc, and iron) sulfides and precious metal ores, besides its role as a reactant or additive in pesticide, rubber, cellulose, and pharmaceutical industries since the 18th century (Spottiswod and Kelly, 1982; Wills, 2006). It is also known to hydrolyze in aqueous solutions and flotation pulps to continually generate toxic species such as carbon disulfide (CS_2), which can accumulate in the flotation plants and thus present a significant hazard on the safety, health and environment (SHE). In recognition of the potential health impacts from the hazardous gases accumulating in the enclosed infrastructures and the chronic exposure to the decomposition products, regulatory bodies are limiting the permissible level of CS_2 in the ambient atmosphere. The permissible limit for CS_2 release has decreased from 10ppm to 1ppm in the US and Canada (OSHA). Measures need to be taken to apply xanthate in a benign and sustainable manner in the flotation operations, reducing the negative SHE impacts. This requires a detailed understanding of the decomposition behavior of xanthate. While extensive studies have been conducted in the past eight decades to understand the interactions between xanthate and sulfide minerals as well as precious metals (Healy, 1984; Poling, 1976; Salamy and Nixon, 1953; Woods, 1976, 1984, 1996), the decomposition behavior remains poorly understood. To develop a more complete understanding of xanthate decomposition, we have taken steady investigations towards examining the decomposition behavior of xanthates under various conditions (e.g., in aqueous solutions in the absence of minerals and in ore pulps under flotation conditions). This paper focuses on Sodium *iso*-Butyl Xanthate (SIBX) decomposition in aqueous solutions in the absence of minerals, which is a control for other conditions.

Decomposition is defined as the breakup of the xanthate anion into ~~pieces~~fragments (such as carbon disulfide or carbonyl sulfide). Dimerization or oxidation of xanthate to dixanthogen ((R-OCS₂)₂) is not included in the definition of decomposition, though it was included in some studies (Rao, 1971). There are a few published studies on xanthate decomposition in aqueous solutions in the absence of minerals (Rao, 1971; Report, 2000). In these studies, researchers applied a similar method called Stopped Flow Technique (SFT) developed by Tornell to investigate the decomposition (Tornell, 1966a, b, 1967). SFT employs UV-vis spectroscopy as the primary technique to track the decrease of xanthate in the aqueous solutions. The amounts of decomposition products generated were derived from the relationship of residual xanthate content as a function of time. This method suffered from several limitations in spite of adopting a meticulous protocol for preparing and measuring the concentrations of solution species. For example, decomposition products in the gas phase could not be identified directly and CS₂ had to be assumed to be the only product in the gas phase. The UV-vis band assignments for xanthate and its relevant compounds (such as xanthic acid or dixanthogen) were not unanimously agreed upon. SFT was not suitable for heterogeneous solutions containing minerals (i.e., ~~in ore pulp of flotation operation~~flotation pulp). Last but not least, the decrease of xanthate in solution might not be solely due to decomposition. Despite ~~of~~ the limitations of SFT, certain key findings have been reported.

Iwasaki et al. (Iwasaki and Cooke, 1958), Finkelstein (Finkelstein, 1967), and Tipman et al. (Tipman and Leja, 1975) indicated that oxygen did not affect decomposition in acidic and alkaline solutions. ~~It~~This permits studying xanthate decomposition under ambient conditions; i.e. exposure to air. Researchers have examined the impact of pH on decomposition more than that of any other factor. It was generally believed that decomposition is greater under acidic

conditions than under alkaline conditions. However, in alkaline solutions, multiple reactions were associated with the xanthate decomposition process, in contrast to the dominance of a single step reaction in acidic solutions. For example, under acidic conditions, xanthate decomposes to CS₂, whereas under alkaline conditions it also forms dioxanthogen (Pomianowski and Leja, 1963), perxanthate (Pomianowski and Leja, 1963; Sun and Forsling, 1997), monothio- and dithio-carbonates (Philip and Fichte, 1960), and trithiocarbonate (Report, 2000). With respect to kinetics, xanthate decomposition was reported to follow a first order law regardless of pH (Ballard et al., 1954; Finkelstein, 1967, 1977; Iwasaki and Cooke, 1958, 1959, 1964; Klein et al., 1960; Majima, 1961). Multiple reactions in parallel or ~~in sequence~~ sequentially (Report, 2000) accompanied the decomposition reaction, but the CS₂ generation was still found to obey the first order kinetics (Finkelstein, 1967, 1977). Nevertheless, it is unclear as to whether the decomposition reaction should be unimolecular (Ballard et al., 1954; Iwasaki and Cooke, 1958, 1959, 1964; Klein et al., 1960) or bimolecular (Majima, 1961). It remains uncertain as to whether there ~~existed~~ exists a maximum decomposition extent as a function of pH. Ballard et al. (Ballard et al., 1954), Klein et al. (Klein et al., 1960) and Iwasaki et al. (Iwasaki and Cooke, 1964) proposed such a maximum when pH reached a certain low level while others did not (Iwasaki and Cooke, 1958, 1959). Under alkaline conditions, Tipman et al. (Tipman and Leja, 1975) found that decomposition remained almost unchanged with pH, while Finkelstein (Finkelstein, 1967, 1977) observed that it still decreased.

Although studies were found on xanthate decomposition in the literature, they are limited and ~~with~~ provide inadequate methods and conflicting results. As explained above, the decomposition was not fully understood in aqueous solutions in the absence of minerals. It is, however, necessary to have sufficient knowledge of decomposition under this control condition

so as to elucidate this behavior under other conditions. This paper reports the study of SIBX decomposition in aqueous solutions in the absence of minerals with a new method markedly different from the SFT. ~~A~~The method was adopted to analyze the decomposition products in the gas phase directly by GC-MS (Gas Chromatography-Mass Spectroscopy). SIBX decomposition was examined as a function of time, xanthate concentration, and pH. One goal of the study was to determine whether the decomposition kinetics could be assessed by analyzing the decomposition products in the gas phase. A second goal was to examine whether or not a maximum decomposition extent exists. A third goal was to discuss and propose probable parallel and sequential reactions that may be responsible for the decomposition behavior across the acid-to-alkaline pH range.

Experimental

Materials

Sodium *iso*-Butyl Xanthate (SIBX, $(\text{CH}_2)_2\text{CHCH}_2\text{OCS}_2\text{Na}$) with $\geq 99\%$ purity was obtained from Cytec Industries. Fresh xanthate solutions were prepared right before each experiment. Reagent Grade CS_2 with $\geq 99.9\%$ purity was purchased from Fisher Scientific. A series of standard solutions of CS_2 with different concentrations in distilled water were prepared to develop a calibration curve for the estimation of the CS_2 generated upon SIBX decomposition. Water used was triple distilled ($\text{EC}=1.5 \mu\Omega^{-1}$). Reagent Grade HCl and NaOH, obtained from Sigma Aldrich, were used to regulate the pH levels of the SIBX solutions.

Method

Our scheme to assess xanthate decomposition under various conditions (e.g., in solution in the absence of minerals or ore pulps under flotation conditions) is shown in Figure 1.

Figure 1. General scheme for measuring decomposition products

A reactor where decomposition takes place is to simulate the desired conditions and accumulate decomposition products. The impact of factors can be examined by modifying the conditions in the reactor. The decomposition products in different phases can be either directly sent to the instrument for measurement, or collected and then subsequently sent for measurement. The instruments for measuring decomposition products in various phases include GC-MS, FTIR, UV-vis, and Raman.

Based on the scheme in Figure 1, the experimental procedure to study decomposition in aqueous solution in the absence of minerals is shown in Figure 2. The reactor is a 10 ml glass vial that can be crimped with an aluminum cap lined with a silicone septum. A Teflon film is deposited at the bottom of septum facing inside the vial. In each test, stock SIBX solution and distilled water were introduced into the vial to obtain a 1 ml SIBX solution at a desired concentration. The temperature was controlled by placing the vial in an incubator. 1 ml of the 9 ml headspace was extracted and transferred to the GC-MS for measurement after a given time. Each vial was used for only one measurement and the above procedure was repeated to prepare another vial for a new measurement.

Figure 2. Experimental scheme for measuring decomposition products in the gas phase

Due to the high selectivity, accuracy and sensitivity, GC-MS was selected to measure the decomposition products in the gas phase. The versatile MPS (multipurpose sampler) developed

for the GC-MS is capable of extracting and transferring the sample in the headspace from a sealed vial to the column. There is an incubator as part of the MPS that can hold the vial at a chosen temperature before the headspace is extracted. This sampler enables direct measurement of the SIBX decomposition products generated in the gas phase. The model of GC-MS used in this study was Agilent 6890GC/5973MS. MPS was from Gerstel. The column was DB-5MS (30 m length, 0.25 mm I.D., and 0.25 μ m film thickness). The temperature program for the column was 35 °C (2 min) + 15 °C/min to 120 °C + 30 °C/min to 300 °C. Other key parameters of the GC-MS during measurements were: split ratio 5:1, injection port temperature 200 °C, and flow rate 1 ml/min. Three variables, namely decomposition time, initial SIBX concentration, and pH, were examined and Table 1 summarizes the details of the experimental program.

Table 1 Experimental program for measurements of SIBX decomposition

Variable	Time [^] (Hours)	pH [*]	SIBX Concentration (wt.%) [#]	Temperature (°C)
Time	0.5, 1, 2, 3, 4, 5, 6, 8, 10, 12, 14, 24	Ca. 6.8	0.05	25, 50 and 70
SIBX Concentration	2	Fixed at 7	0.05, 0.1, 0.25, 0.5, 0.75, 1	50
pH	2	1.5 to 12.5	0.05	25

[^]Counted from when the vial was sealed until the headspace was extracted for GC/MS measurement.

^{*}Represents the initial pH of the solution.

[#] Initial concentration of SIBX solution.

Results and Discussion

Figure 3 shows the GC-MS chromatogram for the decomposition products generated in the gas phase as a function of time (with each chromatogram provide information about the decomposition products after a certain decomposition interval).

Figure 3. GC-MS chromatogram of decomposition products from 0.05 wt.% SIBX solution

The peaks in the chromatogram represented the decomposition species. Only one product was detected for 0.05 wt.% SIBX solution at 25 °C at pH 6.8. It appeared at ca. 1.90 min of retention time and was identified from its mass spectrum as CS₂. Its intensity increased with time.

The decomposition kinetics could thus be studied by determining the amount of CS₂ as a function of time. Evaluation of decomposition kinetics based on CS₂ was consistent with that reported in literature, which assumed that CS₂ was the only decomposition product from xanthate.

Decomposition vs. Time

Using the calibration curve for CS₂, amounts of CS₂ generated from SIBX decomposition were estimated from the peak area. Figure 4 shows the amount of CS₂ from SIBX decomposition as a function of time at 25, 50 and 70 °C.

Figure 4. “CS₂ Generated” vs. Time for 0.05 wt.% SIBX solution at 25, 50 and 70 °C

Below the calculation for the decomposition rate constant based on the CS₂ generated from SIBX decomposition is demonstrated. The SIBX decomposition for the generation of CS₂ can be written as:

----- Eq. 1

Controversy exists with respect to whether the decomposition reaction should be unimolecular (i.e., xanthate and water first form xanthic acid which then decomposes) or bimolecular (i.e., shown by Eq.1). We believe that the bi-molecular reaction is more reasonable. This is because xanthic acid is a moderately strong acid with $pK_a = 2.23$ for butyl xanthic acid (Report, 2000), so under the alkaline, neutral, and weakly acidic conditions, xanthic acid dissociates. Moreover, it was found that molecular xanthic acid was stable in aprotic solvents, therefore there is no reason why it should decompose spontaneously in water (Report, 2000).

The rate of generation of CS₂ can be expressed as:

$$\frac{d[\text{CS}_2]}{dt} = -\frac{d[\text{SIBX}]}{dt} = k_1[\text{SIBX}] - k_2[(\text{CH}_3)_2\text{CHCH}_2\text{OH}][\text{CS}_2][\text{NaOH}]$$

----- Eq. 2

wherein [CS₂], [SIBX], [(CH₃)₂CHCH₂OH], and [NaOH] are the concentrations of CS₂, SIBX, iso-Butanol, and NaOH in solution, respectively; k₁ and k₂ are the reaction rate constants for the forward and reverse directions of Eq. 1.

As duration for the decomposition was short, the amount of CS₂ generated was very low (seen from Figure 4) and a much smaller amount relative to that of SIBX. Therefore, the reverse reaction can be neglected. The final rate equation for the generation of CS₂ can be written as:

$$\frac{d[\text{CS}_2]}{dt} = -\frac{d[\text{SIBX}]}{dt} = k_1[\text{SIBX}]$$

----- Eq. 3

The generation of CS₂ was measured at various SIBX concentrations to confirm that decomposition followed the first order rate law as implied by Eq. 3.

Decomposition vs. Initial SIBX Concentration

Typical concentrations of xanthates used in flotation are 50-500 ppm, according to the type of ores under flotation beneficiation (Spottiswod and Kelly, 1982; Wills, 2006). In the literature, studies of decomposition also encompassed a variety of dosages, some of which were higher than the actual amount that is typically used for flotation. Thus, solutions with initial SIBX concentration ranging from 0.05 to 1% wt.% were investigated. Figure 5 shows the CS₂ generated as a function of the initial SIBX concentration.

Figure 5. “CS₂ Generated” vs. “SIBX Concentration” for 0.05 to 1% wt.% solution at 50 °C for 2h

A linear relationship was seen from the CS₂ generated vs. the initial SIBX concentration, confirming the decomposition to follow the first order kinetics.

Decomposition Kinetics

Decomposition followed the first order rate law, so Eq. 4 could be obtained from Eq. 3:

$$\ln[\text{SIBX}]_t = -k_1 t + \ln[\text{SIBX}]_0$$

----- Eq. 4

wherein $[SIBX]_0$ and $[SIBX]_t$ are the initial (at time=0) and residual (at time=t) SIBX concentration in solution, respectively.

The concentration of SIBX in solution at a certain decomposition time can be calculated based on the CS_2 in the gas phase:

$$\ln[SIBX]_t = \ln([SIBX]_0 - \frac{172}{76} m(CS_2)_{air})$$

----- Eq. 5

wherein $m(CS_2)_{air}$ is the mass of CS_2 in the gas phase. The CS_2 generated will be partitioned between the solution and gas phases. The partition coefficient of CS_2 is difficult to obtain in solutions containing xanthate, as it is continuously decomposing. Thus, the calculation above only accounted for CS_2 that ended up in the gas phase ~~only~~.

Based on Figure 4, the rate constant was calculated to be $9.3 \times 10^{-4} \pm 3.4 \times 10^{-5} \text{ h}^{-1}$ at 25 °C, $1.7 \times 10^{-2} \pm 2.7 \times 10^{-4} \text{ h}^{-1}$ at 50 °C and $1.3 \times 10^{-1} \pm 3.3 \times 10^{-3} \text{ h}^{-1}$ at 70 °C for the 0.05 wt.% SIBX solution at pH 6.8. Compared to the rate constant calculated by previous researchers, we found that it was of the order of 10^{-4} h^{-1} at 25 °C at pH 7 (Finkelstein, 1967, 1977; Tipman and Leja, 1975). The value in our case was higher. Four possible causes are listed below to explain the difference:

- 1) pH level: slightly different in our study (pH=6.8) compared to that in literature (pH=7).
- 2) Experimental techniques: UV-vis spectroscopy tracked the decrease of xanthate in solutions to calculate the decomposition rate constant, while we used GC-MS to directly measure CS_2 in the gas phase. Early studies using the UV-vis spectroscopy suffered from the issue of

ambiguous assignment of bands to xanthate and its related compounds (such as xanthic acid and dioxanthogen), leading to an inaccuracy in the subsequent quantification of the UV-*vis* bands.

3) Type of xanthates: Ethyl, butyl, and amyl xanthates were used in the past studies, while *iso*-butyl xanthate was used throughout our study.

4) Approaches used to calculate the rate constant: in prior work a complex decomposition pathway was presumed, which combined either the uni- or bi- molecular decomposition reaction with other reactions that xanthate was involved in. In the derivation of rate equations, additional assumptions were made which introduce unknown variables. Consequently, the rate constant could be obtained as long as all the other variables were computed together. This approach, adopted by prior researchers, is rather difficult to evaluate the decomposition kinetics. Moreover, their approach was conducted in a reverse manner because they fit the data to their presumed decomposition pathway. This approach could result in misleading interpretations since a set of data could well fit more than one possible pathway. On the contrary, our approach as shown above calculated the decomposition rate constant directly from our experimental data according to Eq.1. With respect to the multiple reactions (occurring in parallel or sequentially with the decomposition reaction) that could affect decomposition, we attempted to find them by varying solution conditions. For example, a list of the probable reactions that could occur in different pH ranges is given below.

Assessment of Decomposition at Different pH Levels

Prior studies discuss the impact of pH relatively more frequently than any other factor. Although pH has been acknowledged to affect decomposition significantly, its impact is still not understood adequately. Our study was aimed to examine the impact of pH over a wider range

compared to other studies in literature that investigated this factor under strictly acidic or alkaline conditions. The CS₂ generated measured from the SIBX solutions as a function of pH between 1.5 and 12.5 is illustrated in Figure 6.

Figure 6. Generation of CS₂ at different pHs from 0.05 wt.% SIBX solution

The CS₂ generation profile indicates that the decomposition was higher under acidic conditions. A maximum decomposition extent was observed at ca. pH 2.2. This observation was in accord with the findings from several researchers (Ballard et al., 1954; Iwasaki and Cooke, 1964; Klein et al., 1960). Notably, while we could confirm the occurrence of this maximum in our study using GC-MS, it could not be reliably observed in SFT using UV-*vis* spectroscopy.

CS₂ generation was lower at pH levels above this maximum and decreased moderately as pH continued to increase beyond this. Such a negligible decrease in the CS₂ generation at high pH agreed with Finkelstein's result (Finkelstein, 1967, 1977), in which the decomposition was shown to decrease even though the decrease was minor.

In order to understand ~~how decomposition changes vs. pH may have been due to different~~the decomposition mechanisms at different pH levels, ~~investigating investigation of the~~ probable parallel or sequential reactions ~~would be~~is required. ~~However at present we could only reasonably propose the multiple reactions associated in the decomposition process at different pH levels. We elaborate~~Before any experimental efforts are taken, these plausible parallel or sequential reactions accompanying the basic decomposition reaction (Eq. 1) are proposed as below:

1. At neutral pH (Region III) the decomposition followed:

----- Eq. 1

2. When pH decreased, the decomposition of SIBX can be rewritten as:

----- Eq. 6

This explains why decomposition increased when pH decreased (Region II).

However, when pH further decreased to ca. 2.2, an additional reaction was assumed to occur:

316 ----- Eq. 7

317 According to this reaction, SIBX would be stabilized and CS₂ generation would
 318 consequently be less at lower pH (Region I). Eq. 7 is the reaction for the formation of a xanthic
 319 acid-like compound (CH₃)CHCH₂OCS₂⁻H⁺ or the protonated form of the xanthic acid that could
 320 stabilize xanthate anion and prevent the decomposition (Ballard et al., 1954; Iwasaki and Cooke,
 321 1964; Klein et al., 1960).

322 3. When pH increased (i.e. OH⁻ increased), the OH⁻ ions could inhibit Eq. 1 from occurring,
 323 so the generation of CS₂ would be reduced. Furthermore, the CS₂ generated would start
 324 interacting with OH⁻ via (Report, 2000):

325 ----- Eq. 8

326 Combining Eq. 8 with Eq. 1, SIBX decomposition in weakly alkaline solution can be
 327 expressed as:

329 ----- Eq. 9

330 This leads to less CS₂ generated compared to that under neutral or acid conditions.

331 When pH further increases, CS₂ further interacts with OH⁻ via (Report, 2000):

332 ----- Eq. 10

333 Combining Eq. 10 with Eq. 1, decomposition in strong alkaline solutions can be
334 expressed as:

335 ----- Eq. 11

336 Eq. 9 and 11 explain Region IV. Under strong alkaline conditions, CS₂ will no longer be
337 generated when Eq. 10 dominates.

338 | The above multiple reactions occurring in parallel and sequential^{ly} provide a rationale for
339 the decomposition behavior under different pH conditions. They clarify the discrepancies in
340 literature (e.g., whether there was a maximum and whether decomposition still decreased in
341 alkaline solution). [Figure 7](#) shows a schematic of the likely types of compounds at different pH
342 levels based on the above reactions. Compounds such as dixanthogen (Pomianowski and Leja,
343 1963), perxanthate (Pomianowski and Leja, 1963; Sun and Forsling, 1997), and monothio- and
344 dithio- carbonates (Philip and Fichte, 1960) that appear under alkaline conditions are also
345 included.

346

Figure 7. Distribution of xanthate compounds in different pH regions;

CS_2 : carbon disulfide; $R-OCS_2^-$: xanthate ion; $R-OCS_2H$: xanthic acid; $R-OCS_2H^+$: xanthic acid-like compound; $R-OH$: alcohol; $(R-OCS_2)_2$: dioxanthogen; $R-OCS_2O^-$: perxanthate; CO_2S^{2-} : monothiocarbonate; COS_2^{2-} : dithiocarbonate; CS_3^{2-} : trithiocarbonate; S^{2-} : sulfide

Conclusions

Compared to the SFT method based on UV-vis spectroscopy, our GC-MS based method provided a direct approach for studying xanthate decomposition behavior and clarified previous discrepancies. The decomposition kinetics was re-evaluated by calculations based on the CS_2 measured in the gas phase. The impact of crucial factors such as pH could be investigated in-depth using this method. A systematic analysis over a wide range of pH was rationalized in terms of multiple reactions that occur in parallel and sequentially along with the decomposition reaction. Features such as the decomposition maximum at low pH were confirmed and a plausible explanation offered. This study may be used as the basis for devising possible measures

that could be taken to mitigate decomposition (e.g., by modifying operation parameters to reduce xanthate decomposition without affecting its performance). It is also a control for further studies of decomposition under flotation conditions.

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445 Supplement Information

446 1. Standard Calibration Equation for CS₂ (Carbon Disulfide)

Magnitude of Peak Area	Calibration Equation:	
	Mass (mg/ml) = Slope x Peak Area + Intercept	
	Slope (x10 ¹¹)	Intercept
10 ⁵	2.38	2.6E-06
10 ⁶	2.50	1.6E-05
10 ⁷	3.15	-1.34E-04
10 ⁸	4.26	-2.58E-03

447 **In our tests the headspace in the vial is 9ml.*

448 2. CS₂ Generated from 0.05wt.% SIBX Solution at 25, 50 and 70°C up to 4 hours **(for Figure 4)**

Time (h)	25°C			
	Peak Area	Mass (mg)	Average Mass (mg)	Error
0.5	1.32E+05	5.16E-05	5.14E-05	9.92E-08
	1.30E+05	5.12E-05		
	1.31E+05	5.14E-05		
1	4.89E+05	1.28E-04	1.26E-04	8.58E-07
	4.75E+05	1.25E-04		
	4.80E+05	1.26E-04		
2	1.32E+06	4.40E-04	4.40E-04	3.97E-07
	1.32E+06	4.41E-04		
	1.31E+06	4.39E-04		
3	1.97E+06	5.86E-04	5.88E-04	5.01E-06
	2.02E+06	5.98E-04		
	1.94E+06	5.81E-04		
4	2.76E+06	7.64E-04	7.63E-04	2.91E-06
	2.77E+06	7.68E-04		

	2.73E+06	7.58E-04		
Time (h)	50°C			
	Peak Area	Mass (mg)	Average Mass (mg)	Error
0.5	6.35E+06	1.57E-03	1.57E-03	7.79E-06
	6.29E+06	1.56E-03		
	6.41E+06	1.59E-03		
1	1.45E+07	2.89E-03	2.90E-03	2.61E-05
	1.44E+07	2.87E-03		
	1.47E+07	2.95E-03		
2	2.78E+07	6.69E-03	6.53E-03	8.09E-05
	2.69E+07	6.42E-03		
	2.71E+07	6.49E-03		
3	4.17E+07	1.06E-02	1.07E-02	3.29E-05
	4.20E+07	1.07E-02		
	4.17E+07	1.06E-02		
4	5.40E+07	1.41E-02	1.42E-02	1.02E-04
	5.50E+07	1.44E-02		
	5.39E+07	1.41E-02		
Time (h)	70°C			
	Peak Area	Mass (mg)	Average Mass (mg)	Error
0.5	5.28E+07	1.38E-02	1.37E-02	3.53E-04
	5.47E+07	1.43E-02		
	5.04E+07	1.31E-02		
1	9.83E+07	2.67E-02	2.67E-02	2.44E-04
	9.69E+07	2.63E-02		
	9.99E+07	2.71E-02		
2	1.90E+08	4.98E-02	4.71E-02	2.36E-03
	1.71E+08	4.24E-02		
	1.89E+08	4.92E-02		
3	2.41E+08	6.95E-02	7.06E-02	5.70E-04
	2.45E+08	7.07E-02		
	2.47E+08	7.15E-02		
4	3.07E+08	9.46E-02	8.99E-02	2.43E-03
	2.92E+08	8.89E-02		
	2.85E+08	8.64E-02		

450 3. Calculation of Decomposition Rate Constant

25°C							
Time (h)	CS ₂ Mass (mg)	Δm(SIBX) (mg)	m _t (SIBX) (mg)	[SIBX] _t (mol/L)	ln[SIBX] _t	ln[SIBX] ₀	ln[SIBX] ₀ -ln[SIBX] _t
0.5	5.16E-05	1.17E-04	5.00E-01	2.91E+00	-5.84087505	-5.84064166	0.000233393
	5.12E-05	1.16E-04	5.00E-01	2.91E+00	-5.87087350		0.000231842
	5.14E-05	1.16E-04	5.00E-01	2.91E+00	-5.84087437		0.000232714
1	1.28E-04	2.90E-04	5.00E-01	2.91E+00	-5.84122158	-5.84064166	0.000579925
	1.25E-04	2.83E-04	5.00E-01	2.91E+00	-5.84120829		0.00056664
	1.26E-04	2.86E-04	5.00E-01	2.91E+00	-5.84121305		0.000571391
2	4.40E-04	9.95E-04	4.99E-01	2.90E+00	-5.84263434	-5.84064166	0.001992687
	4.41E-04	9.97E-04	4.99E-01	2.90E+00	-5.84263843		0.001996767
	4.39E-04	9.94E-04	4.99E-01	2.90E+00	-5.84263230		0.001990646
3	5.86E-04	1.33E-03	4.99E-01	2.90E+00	-5.84329770	-5.84064166	0.002656047
	5.98E-04	1.35E-03	4.99E-01	2.90E+00	-5.84335181		0.002710156
	5.81E-04	1.32E-03	4.99E-01	2.90E+00	-5.81327525		0.002633587
4	7.64E-04	1.73E-03	4.98E-01	2.90E+00	-5.84410658	-5.84064166	0.003464921
	7.68E-04	1.74E-03	4.98E-01	2.90E+00	-5.84412190		0.003480247
	7.58E-04	1.71E-03	4.98E-01	2.90E+00	-5.84407695		0.003435291
50°C							
Time (h)	CS ₂ Mass (mg)	Δm(SIBX) (mg)	m _t (SIBX) (mg)	[SIBX] _t (mol/L)	ln[SIBX] _t	ln[SIBX] ₀	ln[SIBX] ₀ -ln[SIBX] _t
0.5	1.57E-03	3.56E-03	4.96E-01	2.89E+00	-5.84778437	-5.84064166	0.007142711
	1.56E-03	3.53E-03	4.96E-01	2.89E+00	-5.84772284		0.007081184
	1.59E-03	3.59E-03	4.96E-01	2.89E+00	-5.8478459		0.007204242
1	2.89E-03	6.55E-03	4.93E-01	2.87E+00	-5.85382025	-5.84064166	0.013178589
	2.87E-03	6.49E-03	4.94E-01	2.87E+00	-5.85370318		0.013061522
	2.95E-03	6.69E-03	4.93E-01	2.87E+00	-5.8541065		0.013464812
2	6.69E-03	1.51E-02	4.85E-01	2.82E+00	-5.8713918	-5.84064166	0.02949325
	6.42E-03	1.45E-02	4.85E-01	2.82E+00	-5.87013491		0.030750152
	6.49E-03	1.47E-02	4.85E-01	2.82E+00	-5.87045229		0.029810634
3	1.06E-02	2.41E-02	4.76E-01	2.77E+00	-5.88993829	-5.84064166	0.049296636
	1.07E-02	2.43E-02	4.76E-01	2.77E+00	-5.89036996		0.049728304
	1.06E-02	2.40E-02	4.76E-01	2.77E+00	-5.88987086		0.049229205
4	1.41E-02	3.20E-02	4.68E-01	2.72E+00	-5.9066798	-5.84064166	0.066038122
	1.44E-02	3.26E-02	4.67E-01	2.72E+00	-5.9080522		0.067410502
	1.41E-02	3.19E-02	4.68E-01	2.72E+00	-5.90648780		0.065846139

70°C							
Time (h)	CS ₂ Mass (mg)	Δm(SIBX) (mg)	m _t (SIBX) (mg)	[SIBX] _t (mol/L)	ln[SIBX] _t	ln[SIBX] ₀	ln[SIBX] ₀ -ln[SIBX] _t
0.5	1.38E-02	3.11E-02	4.69E-01	2.73E-03	-5.90496675	-5.84064166	0.064325088
	1.43E-02	3.24E-02	4.68E-01	2.72E-03	-5.90766101		0.067019351
	1.31E-02	2.96E-02	4.70E-01	2.73E-03	-5.90177011		0.061128456
1	2.67E-02	6.04E-02	4.40E-01	2.56E-03	-5.96929177	-5.84064166	0.128650115
	2.63E-02	5.95E-02	4.41E-01	2.56E-03	-5.96723544		0.126593781
	2.71E-02	6.14E-02	4.39E-01	2.55E-03	-5.97158357		0.130941916
2	4.98E-02	1.13E-01	3.87E-01	2.25E-03	-6.09583473	-5.84064166	0.255193075
	4.24E-02	9.60E-02	4.04E-01	2.35E-03	-6.05394027		0.21329861
	4.92E-02	1.11E-01	3.89E-01	2.26E-03	-6.09264333		0.252001672
3	6.95E-02	1.57E-01	3.43E-01	1.99E-03	-6.21864512	-5.84064166	0.378003458
	7.07E-02	1.60E-01	3.40E-01	1.98E-03	-6.22659187		0.385950213
	7.15E-02	1.62E-01	3.38E-01	1.97E-03	-6.23166346		0.391021806
4	9.46E-02	2.14E-01	2.86E-01	1.66E-03	-6.39951214	-5.84064166	0.558870481
	8.89E-02	2.01E-01	2.99E-01	1.74E-03	-6.35524546		0.514603807
	8.64E-02	1.95E-01	3.05E-01	1.77E-03	-6.33644748		0.495805821

451

452 By plotting $\ln[\text{SIBX}]_0 - \ln[\text{SIBX}]_t$ against time, the slope is the rate constant.

Temperature (°C)	Linear Fit – R ²	Rate Constant or Slope	Standard Error
25	0.98	9.3E-04	3.4E-05
50	0.99	1.7E-02	2.7E-04
70	0.99	1.3E-01	3.3E-03

453

454 4. CS₂ Generated vs. Initial SIBX for 0.05 to 1wt.% solution at 50°C for 2h **(for Figure 5)**

Concentration	Peak Area	Mass (mg)	Average Mass (mg)	Error
0.05	2.65E+07	6.32E-03	6.49E-03	9.79E-05
	2.71E+07	6.49E-03		
	2.77E+07	6.66E-03		
0.1	5.01E+07	1.30E-02	1.34E-02	2.23E-04
	5.28E+07	1.38E-02		
	5.12E+07	1.33E-02		
0.25	1.55E+08	3.63E-02	3.33E-02	1.69E-03

	1.40E+08	3.05E-02		
	1.47E+08	3.32E-02		
	2.44E+08	7.04E-02		
0.5	2.35E+08	6.72E-02	6.69E-02	2.15E-03
	2.24E+08	6.30E-02		
	3.19E+08	9.94E-02		
0.75	3.09E+08	9.54E-02	1.01E-01	4.16E-03
	3.45E+08	1.09E-01		
	4.31E+08	1.42E-01		
1	4.13E+08	1.36E-01	1.40E-01	2.04E-03
	4.27E+08	1.41E-01		

455

456 By plotting mass of CS₂ against time, the linear relationship is obtained.

Slope		Intercept		Linear Fit – R ²
Value	Standard Error	Value	Standard Error	
1.38E-01	1.19E-03	-4.43E-04	9.57E-05	0.99

457

458 5. CS₂ Generated at Different pHs for 0.05wt.% SIBX Solution for 2 hrs at 25°C **(for Figure 6)**

pH	Peak Area	Mass (mg)	Average Mass (mg)	Error
1.69	2.72E+08	8.13E-02	7.22E-02	4.96E-03
	2.28E+08	6.42E-02		
	2.45E+08	7.11E-02		
2.07	3.45E+08	1.09E-01	9.73E-02	6.46E-03
	3.10E+08	9.59E-02		
	2.87E+08	8.69E-02		
2.18	3.52E+08	1.12E-01	1.05E-01	4.24E-03
	3.37E+08	1.06E-01		
	3.14E+08	9.75E-02		
2.30	1.37E+08	2.96E-02	3.57E-02	3.41E-03
	1.55E+08	3.63E-02		
	1.68E+08	4.14E-02		
2.87	1.40E+08	3.05E-02	3.33E-02	1.69E-03
	1.46E+08	3.30E-02		
	1.55E+08	3.63E-02		
3.40	9.21E+07	1.22E-02	2.47E-02	6.28E-03

	1.38E+08	2.98E-02		
	1.44E+08	3.20E-02		
4.78	3.30E+06	8.87E-04	9.83E-04	5.10E-05
	4.07E+06	1.06E-03		
	3.81E+06	1.00E-03		
6.52	2.58E+06	7.24E-04	7.03E-04	4.37E-05
	2.11E+06	6.19E-04		
	2.77E+06	7.66E-04		
8.03	1.18E+06	4.10E-04	4.00E-04	7.71E-06
	1.07E+06	3.85E-04		
	1.15E+06	4.04E-04		
9.67	1.74E+06	5.36E-04	5.34E-04	4.15E-05
	2.05E+06	6.05E-04		
	1.41E+06	4.62E-04		
10.87	7.88E+05	3.21E-04	3.34E-04	1.18E-05
	7.93E+05	3.22E-04		
	9.48E+05	3.57E-04		
12.5	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	0.00E+00	0.00E+00		
	0.00E+00	0.00E+00		

459

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