

Reaction kinetics of carbon dioxide with aqueous solutions of L-Arginine, Glycine & Sarcosine using the stopped flow technique

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Abstract

The use of amino acids as potential solvents for carbon dioxide (CO₂) capture has been considered by a number of researchers. However, very little is known about the kinetics and mechanism of amino acids–CO₂ reactions. In this work, we investigate the reactions of three amino acids (L-Arginine, Glycine and Sarcosine) with CO₂ in aqueous media using stopped-flow conductivity technique. The experiments were performed at temperatures between 293 and 313 K and amino acids concentrations were in the range of 0.05 to 0.2 molar. The overall rate constants (k_{ov}) was found to increase with increased amino acid concentration and solution temperature. Both zwitterion and termolecular mechanisms were used to model and interpret the data. However, the Zwitterion mechanism was found to be the preferred one. From the stopped-flow results at pH around 6, we found that neutral L-Arginine, Glycine and Sarcosine react with CO₂(aq) with $k(\text{M}^{-1}\text{s}^{-1}) = 2.81 \times 10^{10} \exp(-\frac{4482.9}{T(K)})$, $k(\text{M}^{-1}\text{s}^{-1}) = 3.29 \times 10^{13} \exp(-\frac{8143.7}{T(K)})$ and $k(\text{M}^{-1}\text{s}^{-1}) = 3.90 \times 10^{13} \exp(-\frac{7991.0}{T(K)})$ respectively. The corresponding activation energies are 37.28 kJ.mol⁻¹, 67.71 kJ.mol⁻¹ And 66.44 kJ.mol⁻¹ respectively. A comparison between the kinetics of the three amino acids showed that Arginine exhibits highest reaction rate with CO₂ followed by Sarcosine and then Glycine. The technique and results obtained from this work can be used as strong tools in the development of efficient new solvents for the removal of CO₂ from flue and industrial gases.

Keyword

Carbon dioxide; Glycine; Arginine; Sarcosine; Kinetics; Stopped flow technique.

Introduction

Carbon dioxide is thought to be the most important contributor to global warming among other greenhouse gases [1]. The reduction of carbon dioxide emissions is mandatory to keep CO₂ concentration at an acceptable level for human life. The technology of CO₂ post-combustion capture (PCC) is well recognised by governments and industry as an effective way of absorbing 80–90% of CO₂ emissions from fossil fuel-fired power plants [2]. Captured CO₂ can be compressed and stored in depleted oil and gas fields, deep saline aquifers and unmineable coal seams, thereby reducing the amounts of CO₂ emitted to the atmosphere.

Remarkable progress in CO₂ capture processes using reactive chemical solvents has been observed in the last few decades. Alkanolamines, are well known solvents for their ability to selectively absorb CO₂ from natural and flue gases. Although, various solvents have been used to capture CO₂ (such as hot potassium carbonate, chilled ammonia and ionic liquids), the amine-based processes are still the choice in the industry for CO₂ removal owing to their established characteristics [3].

Monoethanolamine (MEA), a first-generation solvent, is known by its low production cost, high selectivity towards CO₂ and fast reaction rate with CO₂. This can reduce the absorber height and ensure a stable operation of the process. However, several drawbacks are linked to MEA, this include high energy requirements for solvent regeneration, lower absorption capacity compared to tertiary amines such as

MDEA and its susceptibility to thermal and oxidative degradation, which forces periodic solvent make up to maintain stable absorption performance. Furthermore, the significant corrosion tendency of MEA results in considerable equipment maintenance costs.

Amino acid salts, represent a new class of chemical absorbents for CO₂ capture usually referred to as aqueous alkaline salts of amino acids. They contain two important functional groups-namely, amine (-NH₂) and carboxylic acid (-COOH). Taurine, which contains a sulfonic group instead of the carboxylic acid group is also considered as an amino acid [4]. It is one of the popular amino acids that have been tested for CO₂ capture. Amino acids have been commercially employed in acidic gas treatment processes, such as the BASF Alkazid solvent and the Giammarco-Vetrocoke (GV) process, which use carbonate solution as an absorbing solvent. Siemens Energy tested a commercial absorbent based on a functional amino acid salt solution in an industrial-scale pilot plant in Germany at 298 K and 313 K. Compared to MEA solution, the amino acid salt solution has near-zero fugitive emissions, less corrosion in equipment materials and very little oxygen degradation [5, 6]. Amino acid salts have drawn significant attention from researchers in the field of CO₂ capture owing to their attractive characteristics [7-15]. Amino acids are known to have low volatility which results in low solvent losses during the regeneration process [16], substantial resistance to oxidative degradation, making them a suitable choice in the treatment of flue gases containing large amounts of oxygen. They bind readily with CO₂ due the presence of a polar side chain within their structure [17]. However, amino acid salts have their own drawback; they precipitate at high concentrations or high CO₂ loading, resulting in a lower mass transfer rate and a possibility of damaging the process equipment [18]. Kumar et al.[7, 8] measured the solubility of CO₂ in taurate solution at 298 K and 313 K at CO₂ partial pressures ranging from 0.1 to 6 kPa. They also investigated the kinetics of CO₂ absorption in taurate and glycine solutions at temperatures using a stirred-cell reactor and determined their respective reaction rate constants. Portugal et al. [19] compared the overall kinetic constant of CO₂ absorption in glycinate and MEA solutions, and found that the absorption rate of CO₂ in glycinate solution is faster than that in MEA solution. Knuutila et al. [20] used a laboratory-scale pilot plant to study the CO₂ absorption kinetics of sarcosinate solution. Although the absorption rate of sarcosinate solution is faster than MEA, they found that sarcosinate requires a higher reflux ratio and desorption temperature than MEA in the reboiler and stripper for CO₂ desorption. Van Holst et al.[10] investigated the apparent rate constants for several amino acid salts at 298K to find suitable absorbents for CO₂ capture. They found that amino acids solutions such as glycinate, proline, sarcosinate and taurate exhibit relatively high reaction rate constants that are similar to monoethanolamine (MEA) solutions. Wei et al. [21] investigated the salt of potassium taurate as potential solvent for use as a high-temperature absorbent for post- combustion CO₂ capture. They found that CO₂ solubility of taurate solutions, measured using a stirred-cell reactor, is comparable to that of alkanolamines at high temperatures. Thee et al [22] studied the kinetics of CO₂ capture with potassium carbonate solutions promoted with various amino acids: Glycine, sarcosine and proline using a wetted-wall column for concentrations up to 2.0 M and temperatures from 40 to 82°C. Their results showed that the addition of 1.0 M glycine, sarcosine and proline accelerates the overall rate of absorption of CO₂ into a 30 wt% K₂CO₃ solvent by a factor of 22, 45 and 14, respectively. Benamor et al [15] studied the reaction kinetics of CO₂ in aqueous blends of N-methyldiethanolamine and glycine using the stopped flow technique and found out that the addition of small amounts of Glycine to MDEA, considerably enhances its reaction rate with CO₂. The molecular structure of Glycine, Arginine and Sarcosine are shown in Figure 1 below:

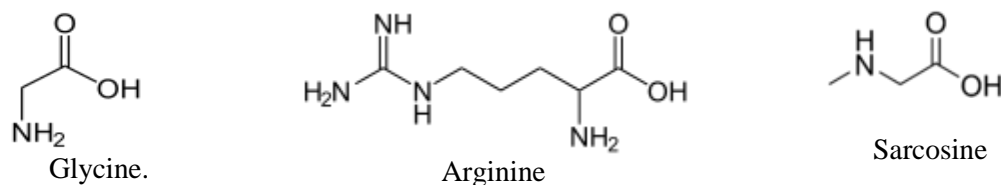


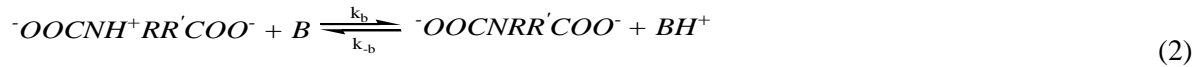
Figure 1: Molecular structure of amino acids used in this study

Several alternative techniques are available for the investigation of reaction kinetics, this include stirred cell, stirred semi-batch, laminar jet absorber, falling film , wetted sphere and stopped-flow technique[23]. Among these techniques, stopped-flow, which is a direct method, has been widely used due to its large coverage of reaction rates and reproducible results[24]. Furthermore, the stopped-flow technique is very useful for screening novel solvents due to its requirement for very small solvent quantities and its experimental procedure[25]. Therefore, in this study, the reaction kinetics of three amino acids with CO₂ were investigated using the stopped-flow technique.

With the exception of the works of Guo et. al [26] and Xiang et. al [27], no prior studies have considered the reactions between glycine and CO₂ and that of Sarcozine and CO₂. However, no kinetic data are available for the reaction of Arginine and CO₂. The main aim of this current work is to investigation the kinetics and mechanisms of aqueous CO₂ reactions with solutions of neutral forms of L-Arginine, Glycine & Sarcosine using stopped flow conductivity technique under different experimental conditions such as temperature, ranging from 298 to 313 K and amine total concentration varying between 0.05 and 0.2 M. The obtained experiments experimental results were modelled using the zwitterion and termolecular mechanisms and the corresponding rate constants and their associated activation energies were evaluated. Furthermore, a comparison between the kinetics of the three the amino acids was performed and a comparison with the published data was provided. In general, this work provides new insight into the fundamental kinetics and mechanism of three amino acids reactions with CO₂, which can be used for the development of new solvent systems for CCS.

CO₂-Amino Acid Reaction Mechanism and Rate Models

Due to similarities in the molecular structure of amino acids and that of primary amines, it can be expected that the CO₂-Amino acid reaction pathway will be similar to that of CO₂-Amine[28]. It is widely accepted that the reaction of CO₂ with amines can be explained by a zwitterionic mechanism. This mechanism as suggested by Caplow et al [29], involves binding of CO₂ with amino group of the primary or secondary amine which results in the formation of a zwitterion. The zwitterion then undergoes rapid deprotonation via H⁺ ions exchange of with water and the other bases until it finally forms a Carbamate.



Applying the steady-state principle to the intermediate zwitterion, the rate of reaction of CO₂ in aqueous solutions of amines can be described as:

$$r_{CO_2} = -k_{ov}[CO_2] = -\frac{k_2[CO_2][AA]}{1+(k_{-1}/(\sum k_{b_i}[B_i])} \quad (3)$$

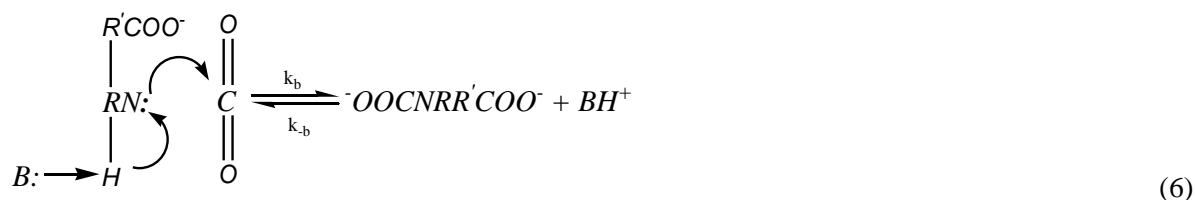
Where the terms in brackets represents the concentrations in M, the term 'B_i' represents the bases, while *k_{bi}* denotes the rate of the deprotonation of the zwitterion by any bases. In case of amino acids, deprotonated amino acid, water molecules and hydroxyl ions acts as the bases. Therefore, the overall reaction rate becomes:

$$k_{ov} = \frac{k_2[AA]}{1+\frac{k_{-1}}{k_{AA}[AA]+k_{OH^-}[OH^-]+k_{H_2O}[H_2O]}} \quad (4)$$

Now by defining new constants as $k_\beta = \frac{k_2 k_{AA}}{k_{-1}}$, $k_{hyd} = \frac{k_2 k_{OH^-}}{k_{-1}}$ and $k_w = \frac{k_2 k_{H_2O}}{k_{-1}}$, then equation 4 can be rewritten as:

$$k_{ov} = \frac{[AA]}{\frac{1}{k_2} + \frac{1}{k_\beta[AA]+k_{hyd}[OH^-]+k_w[H_2O]}} \quad (5)$$

Questioning the validity of the zwitterion mechanism, Crooks and Donnellan [30] proposed a single-step termolecular mechanism. It involves only one step in the reaction process.



Silva and Svendsen [31] further investigated this mechanism and suggested that the reaction progresses by bonding of the CO₂ molecule with the amine which is stabilized by solvent molecules with hydrogen bonds resulting in the formation of loosely bounded complex. They also noted that the carbamate only forms when the amine molecule is in the vicinity of zwitterion. When carbamates are not formed it means the zwitterion has reverted back to free CO₂ and amine. The rate expression analysis of the termolecular mechanism shows that the reaction of CO₂ with amine is second order with respect to amine. Therefore, in this case, equation (3) becomes,

$$r_{CO_2} = k_{ov}[CO_2] = [CO_2][AA]\{\sum k_{b_i}[B_i]\} = [CO_2][AA]\{k_a[AA] + k_w[H_2O] + k_{hyd}[OH^-]\} \quad (7)$$

Nonetheless, whichever mechanism is employed to interpret the data, a carbamate and a protonated base are the generally accepted products of the CO₂ reaction with amine. In this work, both mechanisms were investigated.

Materials and Procedure

Materials

Reagent grade L-Arginine of purity-99%, Glycine of purity 99% and Sarcosine of purity 98% were purchased from Fluka, Riedel de Haen and Aldrich respectively. CO₂ solution was prepared by bubbling analytical grade CO₂ in deionized water for at least half an hour. Throughout the experiments, deionized water was used as solvent.

Procedure

Using a standard stopped-flow apparatus (Hi-Tech Scientific Ltd., UK, Model SF-61DX2) the homogeneous reaction rate between each amino acid (L-Arginine, Glycine and Sarcosine) and the dissolved CO₂ in water was measured. The stopped flow apparatus consists of five major parts namely; sample-handling unit, conductivity-detecting cell, an A/D converter, a microprocessor and a computer with 'Kinetasyst' software. The sample flow circuits are immersed in the water bath where the temperature was controlled using an external water bath Lauda model Alpha RA8 within ± 0.10 K. Fresh saturated solution of CO₂ was prepared by bubbling CO₂ gas in deionized water. The concentration of CO₂ in deionized water was determined according to the Shell method®-SMS 2239-04 using a gas chromatograph (GC-6890 from Agilent). Afterwards, the CO₂ solution was diluted by adding fresh deionized water ensuring that the concentration of the amine was more than 15 times higher than that of CO₂. This was done in order to make sure that a pseudo first order condition with respect to CO₂ is met [32]. Aqueous solutions of the amino acids were also prepared from the deionized water. The CO₂ solution and the amino acid solutions were loaded in two separate syringes. Then, equal doses of both solutions were mixed and pushed pneumatically into the conductivity cell of the stopped flow apparatus using 'Kinetasyst' control software. The final concentration of the amino acids after mixing varied from 0.05 to 0.2 molar. For each experimental run,

aqueous solutions of amino acids and CO₂ were mixed in the stopped-flow apparatus at specified temperatures. The run time of the experiments were varied from 0.5 to 5 seconds depending on the employed temperature. The reaction was then monitored by measuring the change in conductivity, 'Y', as a function of time as described by Knipe et al.[33]. The change in conductivity with respect to time is fitted according to an exponential equation resembling the following first-order kinetic equation:

$$Y = -A\exp(-k_{ov}.t) + Y_{\infty} \quad (8)$$

The term k_{ov} denotes the overall pseudo first order reaction rate constant. In Figure 2, the term 'R' represents the ' k_{ov} '. The average value of three experimental runs was considered for each condition. The error in reproducibility of k_{ov} was less than 3% in all experiments.

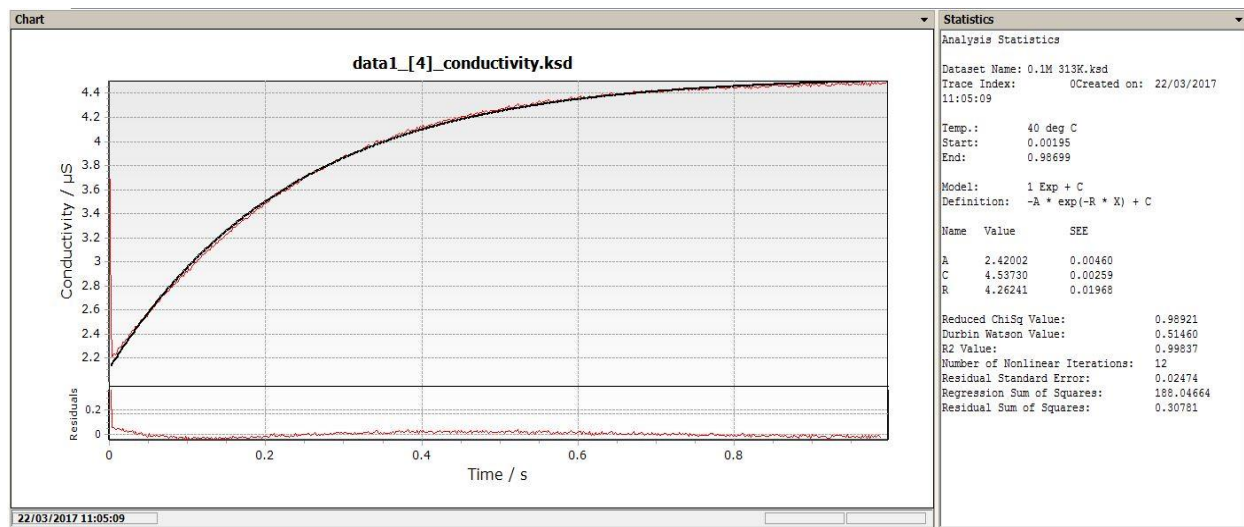


Figure 2: Typical run of 0.1M Glycine with CO₂ at 313K

Results and discussion

Reaction of CO₂ with L-Arginine, Glycine & Sarcosine

The pseudo first order rate constant (k_{ov}) values obtained through the experiments were plotted as function of L-Arginine, Glycine and Sarcosine concentrations at different temperatures as shown in Figure 3. The rate constant values showed progressive increase with increased temperature and amino acid concentration. Due to its slow kinetics, the reaction of the hydroxide ions with CO₂ in aqueous solution to form bicarbonate ion was not considered in the analysis as was already demonstrated in the work of Guo et al[26].

The overall rate constants versus amino acids concentrations were modelled using power law kinetics. It was observed that the rate constants for CO₂-Glycine and CO₂-Sarcosine had average exponents of 0.95 and 0.89 respectively, which indicates that the pseudo first order regime prevails. Hence, it can be assumed that within the concentration range of 0.05 to 0.2M for, the reaction of CO₂ with both Glycine and Sarcosine can be analysed using the zwitterion mechanism [34]. Hence, it is appropriate to fit the obtained data to equation (5). However, using the power law kinetics for the reaction of CO₂ with L-Arginine an order of 1.22 was obtained. Such behaviour suggests that both zwitterion and termolecular mechanism might be appropriate to describe such reaction. Therefore, this reaction can be evaluated using both mechanisms.

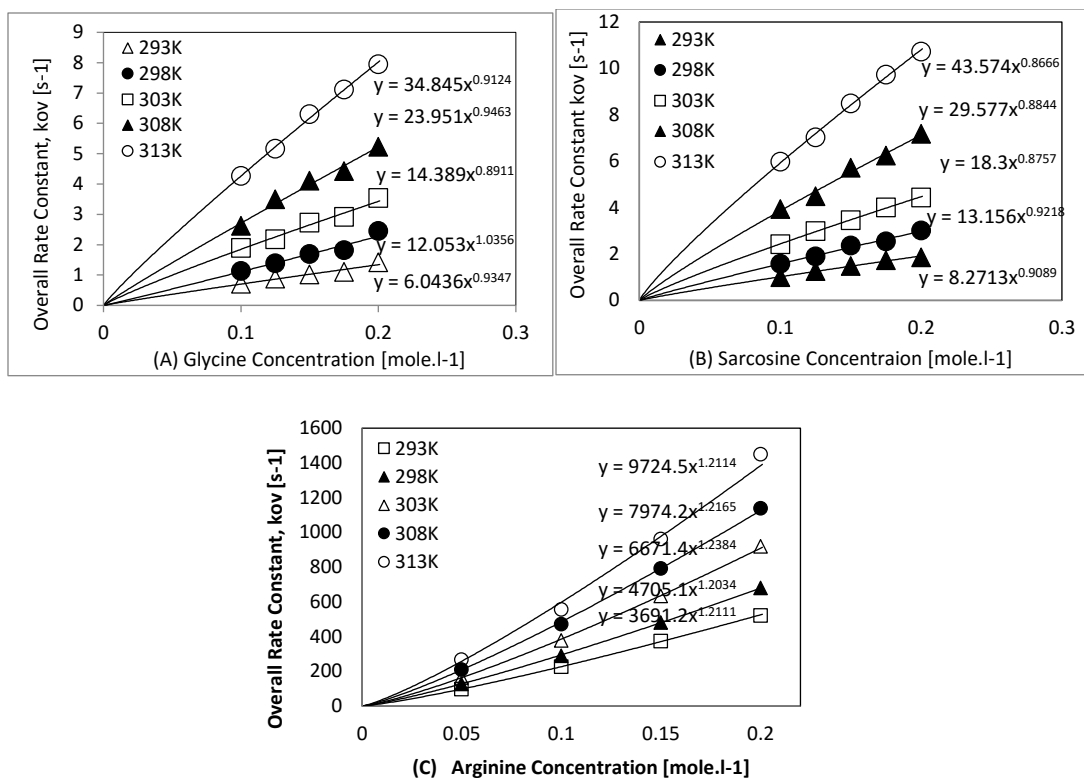


Figure 3: Overall rate constant (k_{ov}) as a function of (A) Glycine, (B) Sarcosine and (C) Arginine concentrations at different temperatures.

Zwitterion Mechanism

The values of k_{ov} obtained from the stopped flow measurements for the reactions between different concentrations of L-Arginine, Glycine and Sarcosine and CO_2 at different temperatures were fitted in accordance with equation (5) using Excel solver for nonlinear regression. For each of the concerned amino acids the individual rate constants were obtained. The generated rate constants for L-Arginine for example are summarized in Table 1.

Table 1: Rate constant for the reaction of CO_2 with L-Arginine based on zwitterion mechanism

Arg	OH $\times 10^3$	H ₂ O $\times 10^{-2}$	k_{ov-exp}	k_{ov-pre}	AAD	k_2	k_β	k_w
mole.l ⁻¹	mole.l ⁻¹	mole.l ⁻¹	s ⁻¹	s ⁻¹	%	m ³ kmole ⁻¹ .s ⁻¹	m ⁶ .kmole ⁻² .s ⁻¹	m ⁶ .kmole ⁻² .s ⁻¹
T=293K								
0.20	1.42	0.53	522.6	531.8	1.8	6224.76	12002.72	4185.54
0.15	1.22	0.54	374.2	368.7	1.5			
0.10	1.00	0.55	226.5	223.3	1.4		AAD%	1.4
0.05	0.71	0.55	98.0	99.0	1.0			
T=298K								
0.20	1.57	0.54	680.7	686.6	0.9	8047.41	15113.40	5536.07
0.15	1.36	0.54	482.2	477.1	1.1			

0.10	1.11	0.55	290.1	289.8	0.1			
0.05	0.79	0.55	128.7	129.1	0.3			
T=303K								
0.20	1.73	0.54	920.7	921.4	0.1	11637.26	20780.80	6479.04
0.15	1.50	0.54	634.1	632.8	0.2			
0.10	1.22	0.55	378.0	378.6	0.2			
0.05	0.86	0.55	165.0	164.9	0.0			
T=308K								
0.20	1.89	0.54	1140.2	1139.9	0.0	13324.22	26266.13	8788.60
0.15	1.63	0.54	792.3	788.9	0.4			
0.10	1.33	0.55	473.0	476.6	0.8			
0.05	0.94	0.55	211.0	210.4	0.3			
T=313K								
0.20	2.05	0.54	1450.0	1400.4	3.4	16378.58	31906.06	10922.45
0.15	1.78	0.54	961.9	970.2	0.9			
0.10	1.45	0.55	558.0	586.9	5.2			
0.05	1.03	0.55	268.0	259.7	3.1			
Overall AAD%								1.1

The concentration of the OH⁻ was estimated according to the relation given by Astarita et al [35].

$$[\text{OH}^-] = \sqrt{\frac{K_w}{K_p} [\text{AA}]} \quad (9)$$

where K_w and K_p represents the dissociation constants of water and the amino acid respectively. Both terms K_w and K_p are expressed as a function of temperature according to the following equation:

$$\ln K = \frac{a}{T} + b \ln T + cT + d \quad (10)$$

The values of the constants in equation (10) are given in the Table 2.

Table 2: Values of equilibrium constants for water

Parameter	a	b	c	d	Validity range	Source
K_w	13445.9	22.4773	0	140.932	0-225°C	Edwards et al.[36]
K_p (Glycine)	-9059.94	16.5101	0.12946	98.09424	5-125°C	Hamborg et al.[37]
K_p (Sarcosine)	-5185.10	0	0	-5.9752	20-60°C	Aronu et al.[38]

The K_p values for arginine which are not available in the open literature were calculated from their corresponding pK_a values experimentally determined in our laboratory by potentiometric titrations at different temperatures. The K_p were then regressed using the following temperature dependent correlation [39]:

$$\ln K_p = A + \frac{B}{T} \quad (11)$$

where the terms A and B are constants. The values of these two constants along with pK_a values obtained at different temperatures for each of amino acids are provided in Table 3.

Table 3: Dissociation constants for L-Arginine in aqueous solution

Amino Acid	pKa at different temperatures				Constants	
	293 K	303 K	313 K	323 K	A	B
L-Arginine	9.11	8.86	8.82	8.65	-9.9729	-3268.3

The natural logarithm of three individual blocks of rate constants presented in Table 1, namely; k_2 , k_β , and k_w were plotted against T^{-1} according to Arrhenius equation and are shown in Figure 4, from which the activation energies were derived for each equation.

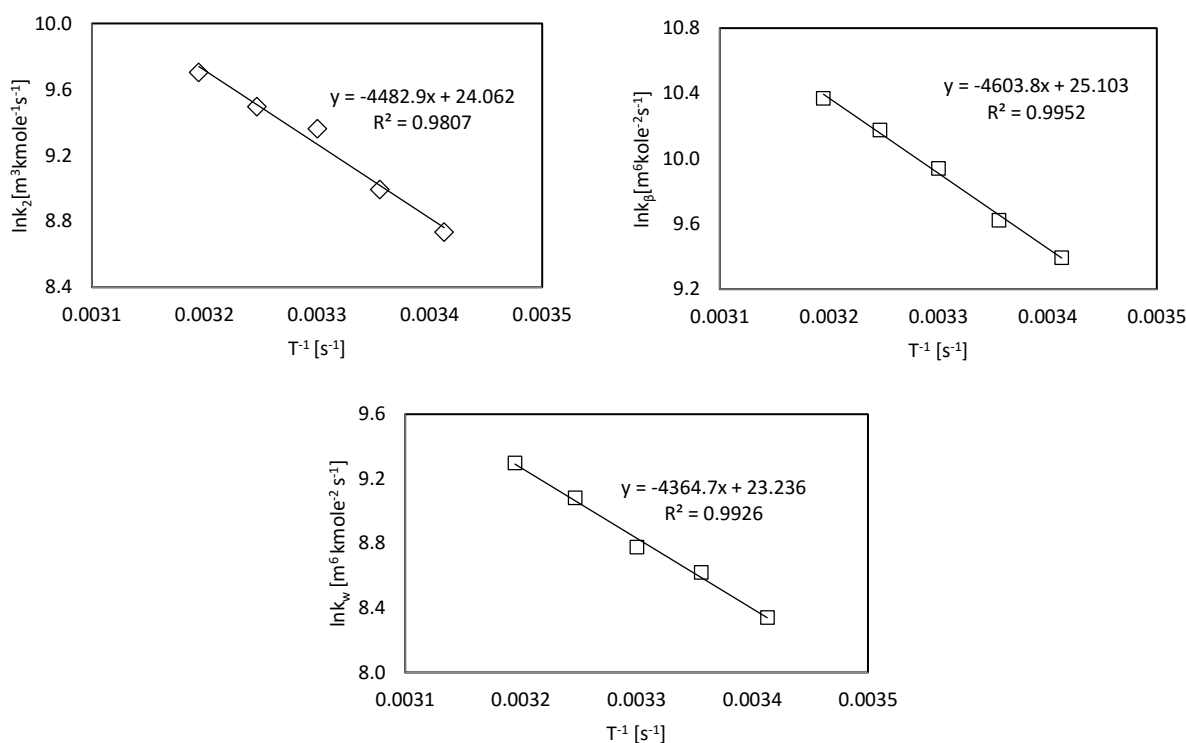


Figure 4: Arrhenius Plot of CO_2 -Arginine Rate Constants

From the obtained straight lines of Arrhenius plots of CO_2 -Arginine, It was noticed that the k_2 showed more variations with the increase in temperature compared to k_β , which in turn was more sensible to temperature than k_w . It is to be noted that the effect of hydroxide ion on the overall reaction rate was initially considered in the regression; however, sensitivity analysis as in the case CO_2 -Arginine showed that OH ion has negligible effect on k_{ov} . The obtained rate expressions for k_2 , k_β , and k_w along with their activation energies are given in Table 4.

Table 4: Summarized kinetic rate constants for CO₂-Arginine over 293-313K based on zwitterion mechanism

Rate	lnk ₀	E _a /R	E _a (kJ/mole)	Equation (k=k ₀ .exp(-E _a /RT))
k ₂ (m ³ .kmole ⁻¹ .s ⁻¹)	24.06	4482.9	37.28	$k_2 = 2.81 \times 10^{10} e^{-\frac{4482.9}{T}}$
k _β (m ⁶ .kmole ⁻² .s ⁻¹)	25.10	4603.8	38.28	$k_\beta = 7.96 \times 10^{10} e^{-\frac{4603.8}{T}}$
k _w (m ⁶ .kmole ⁻² .s ⁻¹)	27.84	4364.7	36.29	$k_w = 1.23 \times 10^{12} e^{-\frac{4364.7}{T}}$

Similarly, the data obtained for CO₂-Glycine and CO₂-Sarcosine were fitted to equation (5) by applying non-linear regression using Excel Solver. The generated rate constants for Glycine and Sarcosine are summarized in Tables 5, and 7 respectively.

Table 5: Rate constants for the reaction of CO₂ with Glycine based on zwitterion mechanism

Gly	OH×10 ²	H ₂ O×10 ⁻²	k _{ov-exp}	k _{ov-pre}	Error	k ₂	k _w
mole.l ⁻¹	mole.l ⁻¹	mole.l ⁻¹	s ⁻¹	s ⁻¹	%	m ³ kmole ⁻¹ .s ⁻¹	m ⁶ .kmole ⁻² .s ⁻¹
T=293K							
0.1000	0.23	0.551	1.42	1.37	3.86	27.56	49.12
0.0875	0.22	0.551	1.10	1.20	8.29		
0.0750	0.20	0.552	1.02	1.02	0.57	AAD%	3.7
0.0625	0.18	0.552	0.88	0.85	2.90		
0.0500	0.17	0.553	0.71	0.68	3.13		
T=298K							
0.1000	0.24	0.551	2.45	2.24	8.44	45.06	80.83
0.0875	0.23	0.551	1.82	1.96	7.84		
0.0750	0.21	0.552	1.69	1.68	0.53	AAD%	3.7
0.0625	0.19	0.552	1.39	1.40	0.84		
0.0500	0.17	0.553	1.13	1.12	1.07		
T=303K							
0.1000	0.25	0.551	3.54	3.54	0.09	71.03	127.89
0.0875	0.24	0.551	2.92	3.10	6.18		
0.0750	0.22	0.552	2.72	2.66	2.43	AAD%	3.4
0.0625	0.20	0.552	2.18	2.21	1.78		
0.0500	0.18	0.553	1.89	1.77	6.32		
T=308K							
0.1000	0.26	0.551	5.23	5.30	1.33	106.27	191.74
0.0875	0.25	0.551	4.42	4.92	4.92		
0.0750	0.23	0.552	4.10	3.98	3.05	AAD%	3.1
0.0625	0.21	0.552	3.49	3.32	5.11		
0.0500	0.19	0.553	2.62	2.65	1.29		
T=313K							

0.1000	0.27	0.551	7.95	8.24	3.58	166.26	300.45	
0.0875	0.25	0.551	7.11	7.21	1.33			
0.0750	0.24	0.552	6.30	6.18	1.82	AAD%	2.0	
0.0625	0.21	0.552	5.17	5.15	0.21			
0.0500	0.19	0.553	4.26	4.13	3.16			
Overall AAD%								3.2

By applying the zwitterion mechanism for CO₂-Glycine reaction, it was noticed that the effects of hydroxyl ion (k_{hyd}) and the catalytic contribution of Glycine in the formation of carbamate (k_{β}) were negligible. In other words, only the effects of k_2 and k_w were found to be important. Using the data presented in Table 5, the natural logarithm of individual blocks of rate constants k_3 and k_w were plotted against the T^{-1} for Glycine in order to obtain the Arrhenius plots and they are shown in Figure 5.

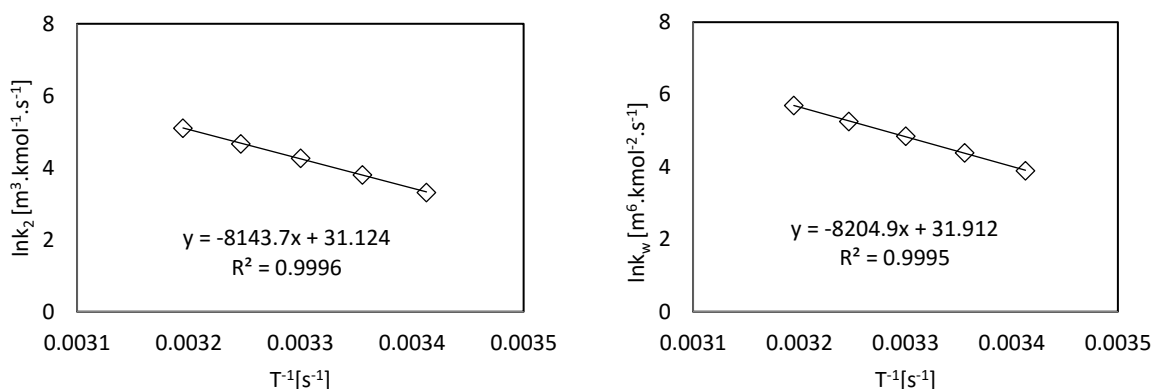


Figure 5: Arrhenius Plots of CO₂-Glycine rate constants

From Arrhenius plots of CO₂-Glycine reaction, the rate expressions for k_2 and k_w were obtained along with their corresponding activation energies and are summarized in Table 6.

Table 6: Summarized kinetic rate constants for CO₂-Glycine over 293-313 K based on zwitterion mechanism

Rate	$\ln k_0$	E_a/R	E_a (kJ/mole)	Equation ($k=k_0.\exp(-E_a/RT)$)
k_2 ($m^3.kmole^{-1}.s^{-1}$)	31.12	8143.7	67.71	$k_2 = 3.29 \times 10^{13} e^{-\frac{8143.70}{T}}$
k_w ($m^6.kmole^{-2}.s^{-1}$)	31.92	8204.9	68.22	$k_w = 3.52 \times 10^{13} e^{-\frac{8204.90}{T}}$

Table 7: Rate constant for the reaction of CO₂ with Sarcosine based on zwitterion mechanism

Sar	$OH \times 10^2$	$H_2O \times 10^{-2}$	k_{ov-exp}	k_{ov-pre}	Error	k_2	k_{hyd}	k_w
$mole.l^{-1}$	$mole.l^{-1}$	$mole.l^{-1}$	s^{-1}	s^{-1}	%	$m^3.kmole^{-1}.s^{-1}$	$m^6.kmole^{-2}.s^{-1}$	$m^6.kmole^{-2}.s^{-1}$
T=293K								
0.1000	0.36	0.550	1.86	1.96	5.42	56.67	25.17	38.13
0.0875	0.33	0.551	1.74	1.72	1.17			
0.0750	0.31	0.551	1.49	1.47	1.30		AAD%	2.7

0.0625	0.28	0.552	1.27	1.23	3.39			
0.0500	0.25	0.553	1.00	0.98	2.06			
T=298K								
0.1000	0.38	0.550	3.02	3.03	0.35	87.85	38.71	58.92
0.0875	0.35	0.551	2.55	2.65	3.99			
0.0750	0.32	0.551	2.37	2.27	4.09		AAD%	2.6
0.0625	0.30	0.552	1.91	1.89	0.58			
0.0500	0.27	0.553	1.58	1.52	4.03			
T=303K								
0.2	0.39	0.550	4.44	4.60	3.50	133.49	58.53	89.36
0.175	0.37	0.551	4.01	4.02	0.34			
0.15	0.34	0.551	3.46	3.45	0.35		AAD%	2.6
0.125	0.31	0.552	2.99	2.87	3.75			
0.1	0.28	0.553	2.42	2.30	5.18			
T=308K								
0.2	0.41	0.550	7.18	7.27	1.26	211.29	92.31	141.25
0.175	0.38	0.551	6.24	6.36	1.89			
0.15	0.35	0.551	5.71	5.45	4.63		AAD%	3.4
0.125	0.32	0.552	4.49	4.54	1.21			
0.1	0.29	0.553	3.94	3.63	7.79			
T=313K								
0.2	0.42	0.550	10.72	11.10	3.50	322.88	140.77	215.67
0.175	0.39	0.551	9.73	9.71	0.22			
0.15	0.36	0.551	8.50	8.32	2.09		AAD%	2.9
0.125	0.33	0.552	7.03	6.93	1.38			
0.1	0.30	0.553	5.98	5.55	7.17			
Overall AAD%								2.8

By applying the zwitterion mechanism for CO₂-Sarcosine reaction, the effect of hydroxyl ion (k_{hyd}) was found to be significant in the formation of carbamate unlike the cases of CO₂-Arginine reaction and CO₂-Glycine. However, the catalytic contribution of Sarcosine in the formation of carbamate (k_{β}) was found to be negligible. The Arrhenius plots and the rate expressions of the individual rate constants k_2 , k_{hyd} and k_w were then obtained and are shown in Figure 6. The corresponding rate expressions and associated activation energies are given in Table 8.

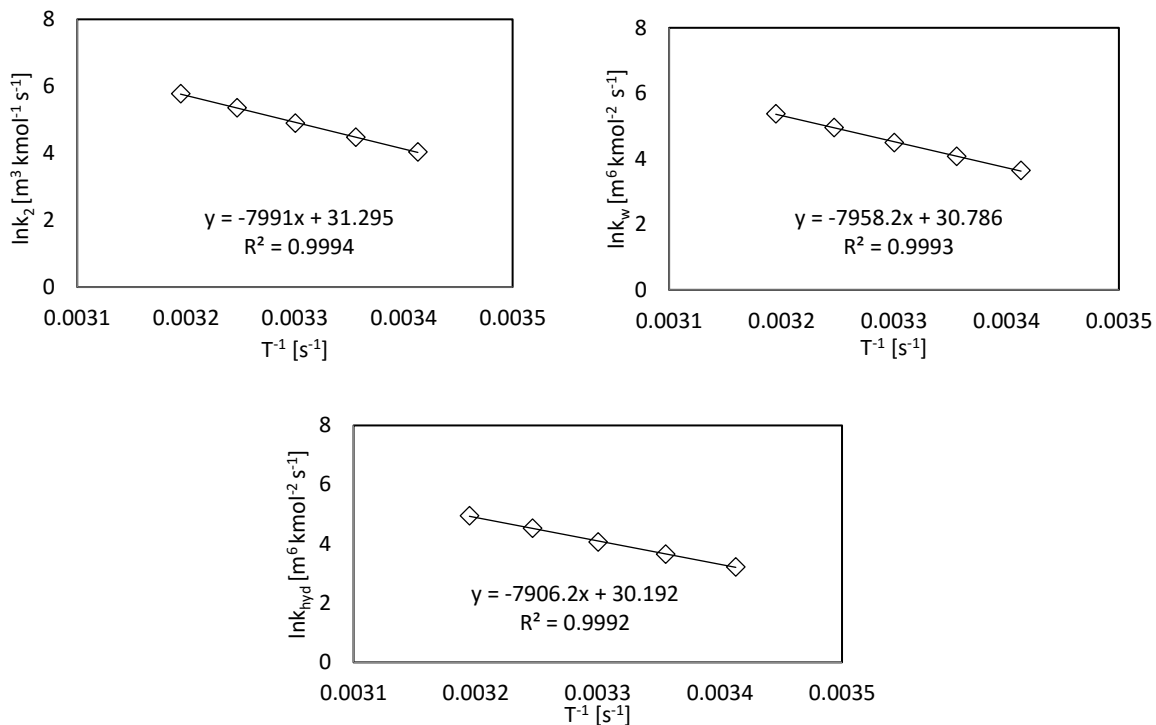
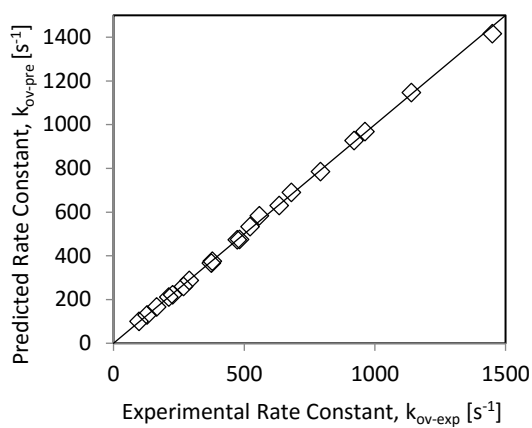


Figure 6: Arrhenius Plots of CO₂-Sarcosine rate constants

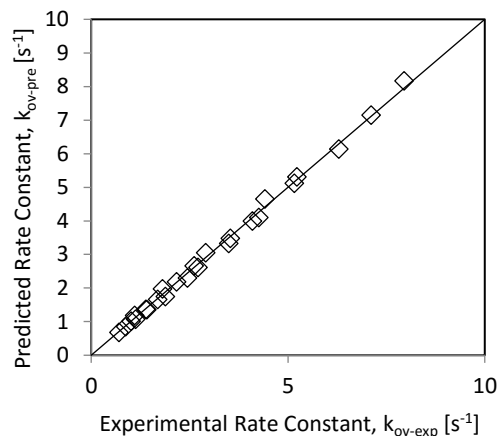
Table 8: Summarized kinetic rate constants for CO₂-Sarcosine over 293-313 K based on zwitterion mechanism

Rate	lnk ₀	E _a /R	E _a (kJ/mole)	Equation (k=k ₀ .exp(-E _a /RT))
k ₂ (m ³ .kmole ⁻¹ .s ⁻¹)	31.30	7991.00	66.44	$k_2 = 3.90 \times 10^{13} e^{-\frac{7991.00}{T}}$
k _{hyd} (m ⁶ .kmole ⁻² .s ⁻¹)	30.19	7906.20	65.73	$k_{hyd} = 1.90 \times 10^{13} e^{-\frac{7906.20}{T}}$
k _w (m ⁶ .kmole ⁻² .s ⁻¹)	30.79	7958.20	66.16	$k_w = 2.35 \times 10^{13} e^{-\frac{7958.20}{T}}$

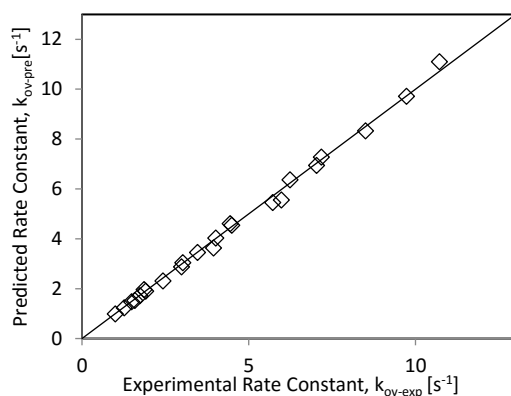
Furthermore, the validity of the zwitterion rate model to represent the experimental data was verified by plotting the predicted overall rate constant i.e. k_{ov-pre} values against the experimental one for all three amino acids (see Figure 7). For the three cases; L-Arginine, Glycine and Sarcosine, It is evident that the adopted rate model along with the extracted blocks of individual rate constants perfectly represent the experimental results with AAD of 1.1 %, 3.2 % and 2.8 % for each case respectively.



(A) Case of L-Arginine,



(B) Case of Glycine



(C) Case of Sarcosine

Figure 7: Predicted vs experimental rate constants for different amino acids

Termolecular Mechanism

The kinetics of CO₂ with the L-Arginine was further investigated using the Termolecular mechanism. k_{ov} values were regressed using Excel solver to generate the individual rate constants according to Equation (7). However, prior to any regression work, the applicability of the termolecular mechanism was verified. To do this, knowing that L-Arginine concentration is low enough to assume that the concentration of water is constant, Equation (7) was reduced to the following [40]:

$$\frac{k_{ov}}{[AA]} = k_a[AA] + k_w[H_2O] \quad (9)$$

By plotting $k_{ov}/[AA]$ against $[AA]$ as shown in the Figure 8, straight lines were obtained which indicates that the termolecular mechanism can be used to interpret the data. The generated rate constants are presented in Table 9.

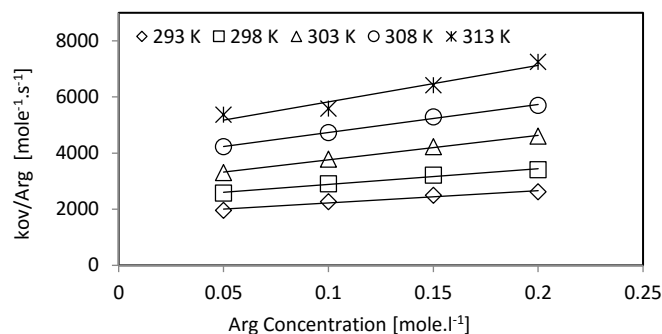


Figure 8: $k_{ov}/[\text{Arginine}]$ vs $[\text{Arginine}]$

Similar procedure was followed for the cases of Glycine and Sarcosine. However, the obtained $k_{ov}/[\text{AA}]$ against $[\text{AA}]$ plots could not yield any satisfactory relationship reaffirming that the single step termolecular mechanism might be used [34].

Table 9: Rate constant for the reaction of CO₂ with Sarcosine based on termolecular mechanism

Arg	OH	H ₂ O	k_{ov-exp}	k_{ov-pre}	Error	k_a	k_w
mole.l ⁻¹	mole.l ⁻¹	mole.l ⁻¹	s ⁻¹	s ⁻¹	%	m ³ .kmole ⁻¹ .s ⁻¹	m ⁶ .kmole ⁻² .s ⁻¹
T=293K							
0.2	0.0014	53.55	522.62	534.02	2.18	4823.74	31.84
0.15	0.0012	54.04	374.18	366.67	2.01		
0.1	0.0010	54.53	226.46	221.88	2.02	AAD%	1.98
0.05	0.0007	55.02	98.00	99.66	1.69		
T=298K							
0.2	0.0016	53.55	680.74	689.99	1.36	6098.86	41.64
0.15	0.0014	54.04	482.19	474.80	1.53		
0.1	0.0011	54.53	290.13	288.07	0.71	AAD%	1.11
0.05	0.0008	55.02	128.74	129.81	0.83		
T=303K							
0.2	0.0017	53.55	920.68	927.55	0.75	9308.79	51.84
0.15	0.0015	54.04	634.05	629.65	0.70		
0.1	0.0012	54.53	378.00	375.75	0.59	AAD%	0.64
0.05	0.0009	55.02	165.00	165.87	0.53		
T=308K							
0.2	0.0019	53.55	1140.21	1147.42	0.63	10708.79	67.14
0.15	0.0016	54.04	792.30	785.17	0.90		
0.1	0.0013	54.53	473.00	473.18	0.04	AAD%	0.45
0.05	0.0009	55.02	211.00	211.46	0.22		
T=313K							
0.2	0.0020	53.55	1450.00	1415.61	2.37	13327.72	82.40

0.15	0.0018	54.04	961.87	967.79	0.62		
0.1	0.0014	54.53	558.00	582.58	4.40	AAD%	2.60
0.05	0.0010	55.02	268.00	259.98	2.99		
Overall AAD%							1.35

The obtained fitting results for CO₂-Arginine reaction using termolecular mechanism showed that hydroxyl ion (k_{hyd}) had a negligible effect similar to the results obtained using the zwitterion mechanism. Only amino acid and water concentrations effects (k_a and k_w) were found to be significant. The natural logarithm of the individual rate constants k_a and k_w where plotted against T^{-1} according to Arrhenius equation as shown in Figure 9. The activation energy of each reaction was determined and the obtained rate expressions for k_a and k_w are summarized in Table 10.

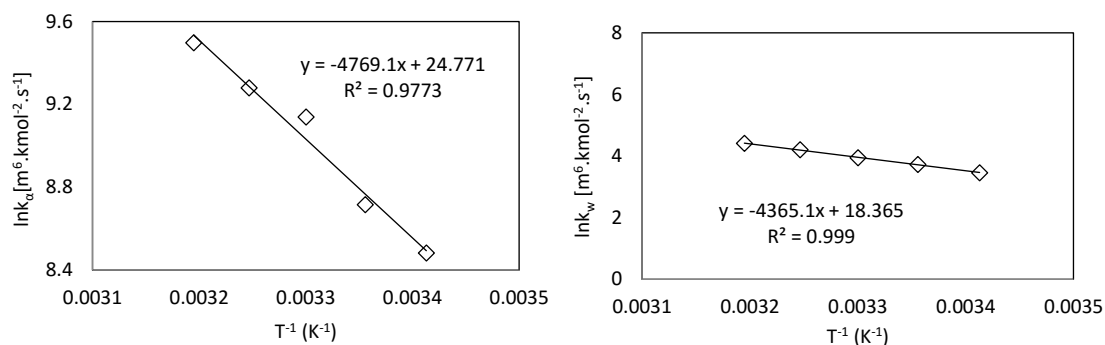


Figure 9: Arrhenius Plot of CO₂-Arginine individual rate constants based on termolecular mechanism

Table 10: Summarized kinetics of CO₂-Arginine over 293-313 K based on termolecular mechanism

Rate	Ln k_0	E_a/R	E_a (KJ/mole)	Equation ($k = k_0 \cdot \exp(-E_a/RT)$)
k_a ($m^6 \cdot kmole^{-2} \cdot s^{-1}$)	24.77	4769.0	39.65	$k_a = 5.72 \times 10^{10} e^{-\frac{4769.00}{T}}$
k_w ($m^6 \cdot kmole^{-2} \cdot s^{-1}$)	18.36	4365.0	36.29	$k_w = 9.41 \times 10^7 e^{-\frac{4365.00}{T}}$

Using the generated individual rate constants, the predicted overall rate constant values were compared to the experimental ones as shown in Figure 10. An excellent agreement was observed between both of them with an AAD of 1.35 % which is very close the AAD obtained in case of zwitterion mechanism (1.12 %), which indicates that the proposed termolecular mechanism can be also used to interpret the experimental data. Furthermore, analysis of the activation energies of k_w based on the two models showed that E_a was identical for both models (36.29 kJ/mole). Based on this, we conclude that both reaction mechanisms can be used to explain the CO₂-Arginine reaction. However, it is well known that, there is one basic Guanidinium group in their side chain within the structure of L-Arginine[41] which can add up a step towards the formation of carbamates. Therefore, it can be suggested that the CO₂-Arginine reaction can be better explained by the two step zwitterion mechanism rather to that of the single step termolecular mechanism.

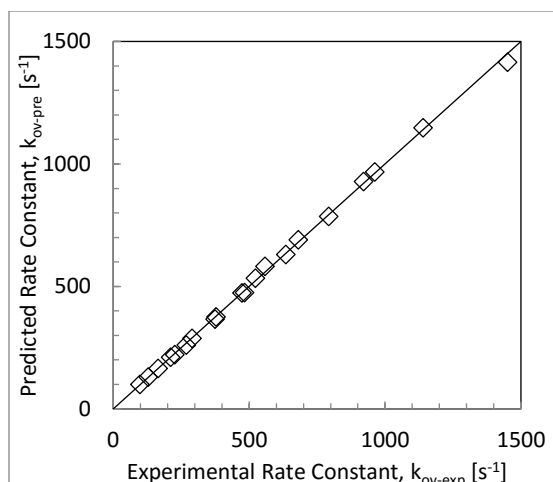


Figure 10: Predicted versus experimental rate constants of L-Arginine based on termolecular mechanism

On the basis of the results obtained previously, it can be proposed that all three amino acids; i.e. Glycine, Sarcosine and L-arginine reactions with CO₂ can be explained by the zwitterion mechanism. The obtained experimental k_{ov} data for both Glycine and Sarcosine reaction with CO₂ could be successfully fitted using zwitterion model with an AAD% of 3.2 and 2.8%. While, the k_{ov} data for the reaction of L-Arginine with CO₂ could be fitted to both termolecular and the zwitterion models. However, due to the presence of the guanidinium group it can be suggested that CO₂-Arginine reaction is more inclined to undergo a two-step zwitterion mechanism. The suggested model and the rate expressions for the each of three amino acids are summarized in Table 11.

Table 11: Summary of reaction mechanism and rate expressions for three amino acids

Amino Acid	Mechanism	Rate Expressions (M ⁻¹ s ⁻¹)
L-Arginine	Zwitterion	$k_2 = 2.81 \times 10^{10} e^{-\frac{4482.9}{T}}$
		$k_\beta = 7.96 \times 10^{10} e^{-\frac{4603.8}{T}}$
		$k_w = 1.23 \times 10^{12} e^{-\frac{4364.7}{T}}$
	Termolecular	$k_a = 5.72 \times 10^{10} e^{-\frac{4769.00}{T}}$
		$k_w = 9.41 \times 10^7 e^{-\frac{4365.00}{T}}$
Glycine	Zwitterion	$k_2 = 3.29 \times 10^{13} e^{-\frac{8143.70}{T}}$
		$k_w = 3.52 \times 10^{13} e^{-\frac{8204.90}{T}}$
Sarcosine	Zwitterion	$k_2 = 3.90 \times 10^{13} e^{-\frac{7991.00}{T}}$
		$k_{hyd} = 1.90 \times 10^{13} e^{-\frac{7906.20}{T}}$
		$k_w = 2.35 \times 10^{13} e^{-\frac{7958.20}{T}}$

Comparison between the three Amino Acids

The rate constants of all three amino acids were compared at concentration of 0.2 mole/l and at different temperatures (See Figure 11). It was observed that among the three amino acids, arginine had the highest rate constant. This could be attributed to the presence of an additional basic Guanidinium group that makes the reaction between arginine and CO₂ much faster. The rate constants of Sarcosine and Glycine were very close to each other with sarcosine slightly faster than glycine. Overall, the rate constants of the three amino acids with CO₂ was found to be in the following order :Arginine>Sarcosine>Glycine.

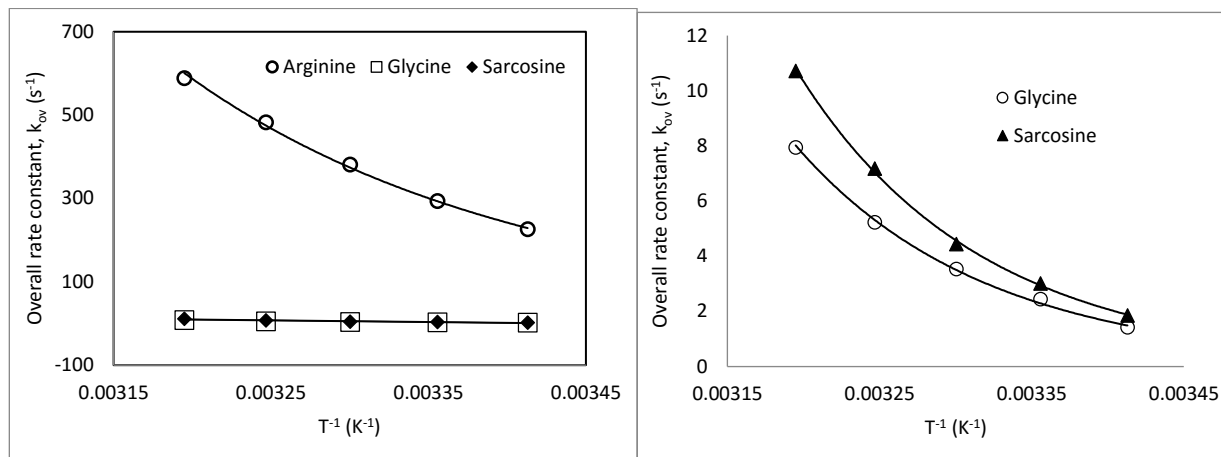


Figure 11: Comparison between reaction rate constants of the three amino acids

Comparison with other works

The obtained kinetics data were compared to the ones available in literatures. For instants, Gou et al.[26] studied the reactions of neutral Glycine with CO₂ and they reported the rate expression of $k(\text{M}^{-1}\text{s}^{-1}) = 8.18 \times 10^{12} \exp\left(-\frac{8624}{T(K)}\right)$ compared to $k(\text{M}^{-1}\text{s}^{-1}) = 3.29 \times 10^{13} \exp\left(-\frac{8143.7}{T(K)}\right)$ in this work. Moreover, the activation energy of neutral Glycine with CO₂ in that study was found to be $71.7 \pm 9.6 \text{ kJmol}^{-1}$ which is comparable to 67.71 kJmol^{-1} determined in this work. Benamor et al. [15] studied the kinetics of reaction of Glycine promoted MDEA with CO₂, deducing a rate expression of $k(\text{M}^{-1}\text{s}^{-1}) = 2.40 \times 10^7 \exp\left(-\frac{3887}{T(K)}\right)$ with an activation energy of 22.95 kJmol^{-1} for Glycine. Clearly, the obtained activation energy is much lower than what is obtained in this study (67.71 kJmol^{-1}). This further indicates that Glycine under the presence of alkanolamines reacts much faster with CO₂ than the neutral Glycine. the rate expression obtained for CO₂-Sarcosine in this work is, $k(\text{M}^{-1}\text{s}^{-1}) = 3.9 \times 10^{13} \exp\left(-\frac{7991}{T(K)}\right)$ with an activation energy of 66.44 kJmol^{-1} which is very close to the one obtained by Xiang et al.[27]. In their study they focussed on the reaction of sodium sarcosinate with CO₂, the rate expressions for sarcosine with CO₂ without sodium was determined to be $k(\text{M}^{-1}\text{s}^{-1}) = 9.5 \times 10^{14} \exp\left(-\frac{7337.02}{T(K)}\right)$ with an activation energy of 61 kJmol^{-1} . Table 12 below summarizes the rate expressions and activation energies obtained in this work and the ones available in the literature, as we can see there is available kinetics data for the CO₂-Arginine reaction; therefore, a comparison is not possible.

Table 12: Comparison of the obtained data with the literature data

Amino Acid	Rate Expressions ($\text{M}^{-1}\text{s}^{-1}$)	E_a (kJ/mole)	Source
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Glycine	$k_2 = 3.29 \times 10^{13} e^{-\frac{8143.70}{T}}$	67.71	This work
	$k_2 = 8.18 \times 10^{12} e^{-\frac{8624}{T}}$	71.7±9.6	Guo et al.[26]
Sarcosine	$k_2 = 3.90 \times 10^{13} e^{-\frac{7991.00}{T}}$	66.44	This Work
	$k_2 = 9.45 \times 10^{14} e^{-\frac{7337.02}{T}}$	61.00	Xiang et al.[27]
Arginine	$k_2 = 2.81 \times 10^{10} e^{-\frac{4482.9}{T}}$	37.28	This work

Conclusion

The kinetics of the CO₂ reaction with aqueous solutions of Glycine, Arginine and Sarcosine were studied using the stopped-flow apparatus at different concentrations and temperature ranging from 293 to 313 K. The three reactions were analyzed using both zwitterion and termolecular mechanism. The obtained results showed that the reactions of Glycine with CO₂ and Sarcosine with CO₂ are best interpreted using the two-step zwitterion mechanism. While the reaction of Arginine with CO₂ can be explained by both zwitterion and termolecular mechanisms. The effect of hydroxyl ion (k_{hyd}) towards the formation of carbamate ion was found to be negligible in the case of CO₂-Glycine reaction and non-negligible in the case of CO₂-Sarcosine and CO₂-Arginine reactions. The contribution of H₂O molecule was found to be significant in the three reactions. The overall rate equations for the three reactions and their temperature dependencies were determined and the associated activation energies were evaluated. On analysing the activation energies of k_2 for all three amino acids, we found that the activation energy of CO₂-Arginine reaction (37.28 kJ/mole) was less than that of CO₂-Sarcosine reactions (66.44 kJ/mole) which in turn was less than that of CO₂-Glycine (67.71 kJ/mole) . This indicates that the reaction between Arginine and CO₂ is faster than CO₂-Glycine and CO₂-Sarcosine reactions and the three reactions follow this order: Arginine > Sarcosine > Glycine. The obtained E_a values of CO₂-Glycine and CO₂-Sarcosine reactions were comparable to those available in the literature; however, no data for the CO₂-Arginine reaction was found in the literature.

Nomenclature

Arg : Arginine

Gly : Glycine

Sar : Sarcosine

AA : Amino Acids

AAD : Average Absolute Deviation

k_2 : Reaction rate constant of the formation of the intermediate zwitterion [m³/mole.s]

k_{-1} : Reaction rate constant of the consumption of the intermediate zwitterion [m³/mole.s]

k_b : Individual reaction rate constants according to zwitterion mechanism [m³/mole.s]

r_{CO_2} : Reaction rate of CO₂ with Amino acid [l/mole.s]

k_{ov} : Overall reaction rates of CO₂ with Amino Acids [s⁻¹]

T : Temperature [K]

t : Time [s]

K_w : Water dissociation constant [-]

$\text{p}K_a$: Dissociation Constants of Amino Acids [-]

$k_{\text{ov-exp}}$: Apparent rate constant [s⁻¹]

$k_{\text{ov-pre}}$: Predicted apparent rate constant [s⁻¹]

E_a	: Activation energy [kJ/mole]
k_β	: Catalytic contribution of Amino Acid in the reaction rate according to the zwitterion mechanism [m ⁶ .kmole ⁻² .s ⁻¹]
k_{hyd}	: Contribution of hydroxyl ion in the reaction rate according to the zwitterion mechanism [m ⁶ .kmole ⁻² .s ⁻¹]
k_w	: Contribution of water in the reaction rate according to zwitterion mechanism [m ⁶ .kmole ⁻² .s ⁻¹]
k	: Rate expression of the amino acid [M ⁻¹ s ⁻¹]

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