Polysulfide-assisted urea synthesis from carbon monoxide and ammonia in water

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ABSTRACT

Efficient conversion of carbon monoxide into urea in an aqueous ammonia solution was demonstrated through coupling with the elemental sulfur reduction to polysulfides. This reaction starts with a simple mixture of carbon monoxide, ammonia, elemental sulfur, and a small amount of hydrogen sulfide for polysulfide formation, enabling an almost complete conversion of 1 atm of carbon monoxide to urea (95–100% yield) within 216, 64, and 32 h at 35 °C, 50 °C, and 65 °C, respectively. Polysulfides control the overall reaction rate while suppressing the accumulation of a by-product, hydrogen sulfide, to less than 1 Pa. These functions follow simple kinetic and thermodynamic theories, enabling prediction-based reaction control. This operational merit, together with the superiority of water as a green solvent, suggests that our demonstrated urea synthesis is a promising option for sulfur utilization beneficial for agricultural production.

INTRODUCTION

Sulfur is a crucial element in agriculture. Besides being a vital nutrient for crop production, sulfur is a common pesticide in the form of elemental sulfur (S^0) (*Griffith, Woodrow & Seiber, 2015*). S^0 is also used as a coating material of urea to regulate urea availability to plants (*Naz & Sulaiman, 2016*; *Wesolowska et al., 2021*), while its oxidation to sulfate (SO_4^{2-}) is applicable to control soil pH (*Roig, Cayuela & Sanchez-Monedero, 2004*). Moreover, sulfuric acid is the mostly used leaching reagent for phosphate extraction from phosphorites (*Sahu et al., 2014*; *Wagenfeld et al., 2019*).

Worldwide, the majority of anthropogenic sulfur is derived from coal and petroleum refinements (*Wagenfeld et al., 2019*; *Rappold & Lackner, 2010*). Although the global sulfur supply currently exceeds the market demand (*Rappold & Lackner, 2010*; *Srivastava, 2012*; *Saleh, 2020*), replacement of fossil fuels with renewable energy sources is expected to lead to a sulfur shortage in the future (*Wagenfeld et al., 2019*). For sustainable agricultural activity involving sulfur, whose market price possibly increases due to its dwindling supply, an economically viable option of sulfur valorization beneficial for agriculture ought to be explored. Such sulfur valorization should also be important in the current sulfur oversupply situation.

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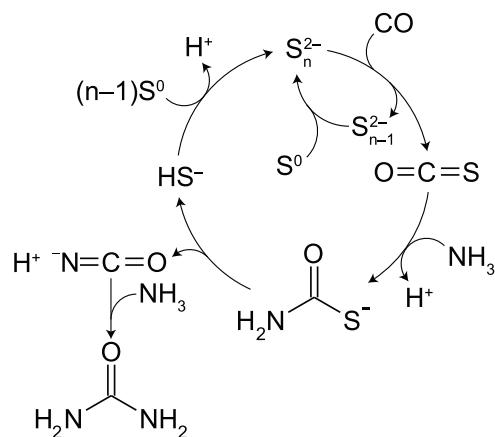
In this article, we demonstrate polysulfide-assisted urea synthesis from carbon monoxide (CO) and ammonia (NH_3) in water. Urea accounts for approximately 50 wt% of the global nitrogen consumption as fertilizer (*Glibert et al., 2006*; IFASTAT, https://www.ifastat.org/). Its production worldwide was over 180 Mt in 2020, and is expected to grow over the next few decades in accordance with the increasing global food demand (*Erisman et al., 2008*; *Bodirsky et al., 2014*). Conventionally, industrial urea synthesis is based on the reaction of carbon dioxide (CO_2) with NH_3 at high temperatures (170–200 °C) and pressures (130–250 bar). Because multi-stage cyclic systems are required to improve the otherwise low reaction efficiency, the overall process is energy consuming, emitting higher amounts of CO_2 than those converted to urea (*Bargiacchi, Antonelli & Desideri, 2019*; *Zendehboudi et al., 2014*; *Rafiee et al., 2018*). CO is a promising alternative to CO_2 because of its superior reactivity (*Diaz, Darko & McElwee-White, 2007*) and growing industrial availability. Highly efficient CO production is now realized on various low-cost electrocatalysts (*Satanowski & Bar-Even, 2020*). The high amount of CO produced through methane steam reforming (*Giddey, Badwal & Kulkarni, 2013*; *Smith, Hill & Torrente-Murciano, 2020*) may also be a practical choice.

There are several reports on the synthesis of urea and urea derivatives from CO and NH_3 or amines with the aid of S^0 (*Franz & Applegath, 1961*; *Franz et al., 1961a*, *1961b*; *Mizuno et al., 2006*, *2007*; *Mizuno, Nakai & Mihara, 2009*; *Peng, Li & Xia, 2006*). However, experiments have typically been conducted in organic solvents; to the best of our knowledge, there are no experimental studies on urea synthesis in water. A difficult intermediate step in water is the formation of thiocarbamate. In certain organic solvents (*e.g.*, N,N-dimethylformamide), thiocarbamates have been shown to form through the binding of the corresponding amines to S^0 *via* the S–S bond cleavage, followed by nucleophilic attack of CO to the resultant thiolate species (*Mizuno et al., 2006*, *2007*; *Mizuno, Nakai & Mihara, 2009*). No thiocarbamate has been formed in this manner when water was used as a solvent (*Mizuno, Iwai & Ishino, 2005*).

In alkaline aqueous solutions, polysulfides (PSs) provide an alternative route to thiocarbamate (Scheme 1). PSs are dissolved sulfur chains (S_n^{2-}; $n = 2–8$) formed from the reaction of S^0 with bisulfide (HS^-) (*Avetisyan, Buchshtav & Kamyshny, 2019*). Because sulfur atoms in PSs are electrophilic at the non-terminal position (*Fukuto et al., 2018*), PSs are susceptible to nucleophilic attack by CO to form carbonyl sulfide (OCS) (*Kamyshny et al., 2003*). OCS is known to readily react with amines to form thiocarbamates, and facilitate a variety of aqueous organic processes (*Huber & Wachtershauser, 1998*; *Leman, Orgel & Ghadiri, 2004*, *2006*). We will show below that these steps occur consecutively in water from a simple mixture of CO, NH_3, S^0, and a small amount of HS^-. Under moderately alkaline pH (10.3–10.5) and temperature (35 °C, 50 °C or 65 °C), an almost complete conversion of 1 atm of CO to urea (95–100% yield) was achieved in the presence of excess amounts of NH_3 and S^0. Importantly, PSs control the rate of OCS formation (*Kamyshny et al., 2003*), which determines the overall rate of urea production.

Scheme 1 Proposed intermediate steps in the polysulfide-assisted urea synthesis from CO and NH$_3$ in water.

Moreover, PSs suppress the accumulation of HS$^-$ by-product through the PS–HS$^-$ equilibrium. Thus, the timescale of urea formation and the resultant H$_2$S concentration can be predicted from kinetic and thermodynamic calculations by parameterizing the PS concentration.

Note that PSs are widely used corrosion inhibitors in the petrochemical industry (*Tiu & Advincula, 2015*). In the presence of oxygen (O$_2$), PSs are oxidized to S^0 at approximately four times the rate of HS$^-$ oxidation (*Steudel, Holdt & Nagorka, 1986*; *Kleinjan, de Keizer & Janssen, 2005*). Although the PS–O$_2$ reaction also generates thiosulfate (S$_2$O$_3^{2-}$) as a by-product, its further oxidation to sulfate (SO$_4^{2-}$) readily proceeds with the aid of sulfide catalysts (*e.g.*, CuS; *Lara et al., 2019*) or by the action of ultraviolet light (*Ahmad et al., 2015*). SO$_4^{2-}$ is a sulfur species directly available to plants (*Lucheta & Lambais, 2012*; *Griffith, Woodrow & Seiber, 2015*; *Fuentes-Lara et al., 2019*). Thus, sulfur is not a mere oxidant facilitating selective urea synthesis from CO and NH$_3$ under mild and non-corrosive conditions. The resultant aqueous suspension is potentially applicable as a sulfur and nitrogen fertilizer source.

MATERIALS AND METHODS

Urea synthesis experiments were conducted in a serum bottle filled with CO (0.33 mmol, 1 atm), S^0 (3.1 mmol), and 5 mL of an aqueous solution of NH$_3$ (14.5 mmol), ammonium chloride (NH$_4$Cl, 1.45 mmol), and sodium hydrogen sulfide (NaHS, 32.5 μmol). NH$_4$Cl was used at a molar ratio of NH$_4$Cl/NH$_3$ = 0.1 to keep the pH at 10.3–10.5 (in the absence of NH$_4$Cl, the pH was 10.7–10.9 after the urea synthesis experiment). NaHS was added for the formation of PSs (($n - 1$)S^0 + NaHS → S$_n^{2-}$ + Na$^+$ + H$^+$) at a concentration of 6.5 mM, which corresponded to 10% of the initial amount of CO. All the reactions involving CO were carefully carried out in a fume hood or a glove box with strict precautions. For more details and product analysis methods, see Materials & Methods in Supplemental Information.

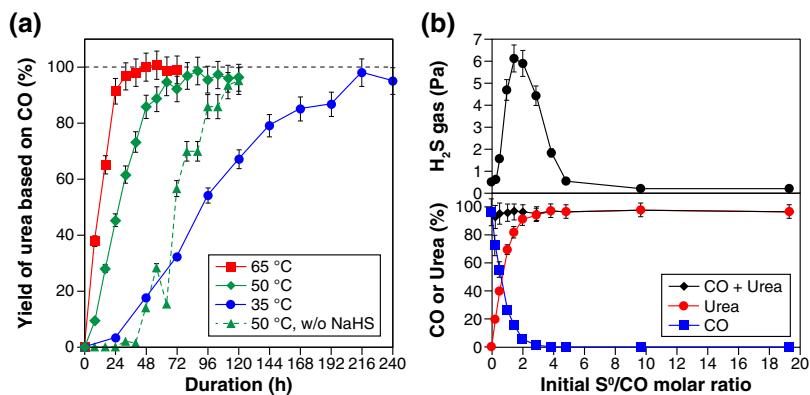



Figure 1 Experimental results for the sulfur-assisted urea synthesis. (A) The yield of urea at 35 °C, 50 °C, and 65 °C. The results obtained without NaHS as a starting material are also shown with triangle symbols connected by dotted lines. (B) Effect of the initial S^0/CO molar ratio on the H_2S gas concentration (top), the yield of urea (bottom), and the amount of CO remaining (bottom) after the 120-h reaction at 50 °C. In this experiment, the initial amount of S^0 was varied between 0 and 6.2 mmol, while that of CO was kept constant at 0.33 mmol.

RESULTS AND DISCUSSION

Experimental results

Figure 1A shows the yield of urea, based on CO, at three different temperatures (*i.e.*, 35 °C, 50 °C, and 65 °C). Urea formation was faster at higher temperatures, reaching 80% yield within 24 h at 65 °C, 48 h at 50 °C, and 168 h at 35 °C. Longer reaction duration led to further urea formation; 95–100% yield of urea was obtained after the 32-, 64-, and 216-h reaction at 65 °C, 50 °C, and 35 °C, respectively (Fig. 1A). Similar time and temperature dependencies were observed at an NH_3 concentration of 5.6 M (Fig. S5). CO_2 was formed as a by-product, but the yield was at most 0.8% under the examined reaction conditions. When no NH_4Cl was added as a starting material, the urea selectivity slightly decreased, while CO_2 formed in higher amount, compared with those in the presence of NH_4Cl under otherwise identical condition. For example, the 120-h reaction at 50 °C in the absence of NH_4Cl resulted in 94 ± 5% yield of urea and 2 ± 0.2% yield of CO_2. No urea was detected when either NH_3 or S^0 was absent and when CO was replaced with CO_2. In the absence of NaHS, the reaction started with a sluggish urea-formation stage (green dotted line in Fig. 1A). This induction period was followed by an accelerated growth of the urea yield that eventually exceeded 90%. The mechanism underlying the sigmoidal-like growth is discussed later.

The initial amount of S^0 had a strong impact on the concentration of H_2S by-product, as well as the yield of urea, as seen in the results obtained after the 120-h reaction at 50 °C (Fig. 1B). With an increase in the S^0/CO molar ratio from 0 to 19.1, the H_2S gas concentration initially exhibited a rapid increase to approximately 6 Pa, followed by a decrease to a value less than 1 Pa at the S^0/CO molar ratio of 4.8, and then reached a steady value (ca. 0.2 Pa) at higher S^0/CO molar ratios. As for urea, the yield increased significantly when the S^0/CO molar ratio was between 0 and 2 at the expense of CO (Fig. 1B).

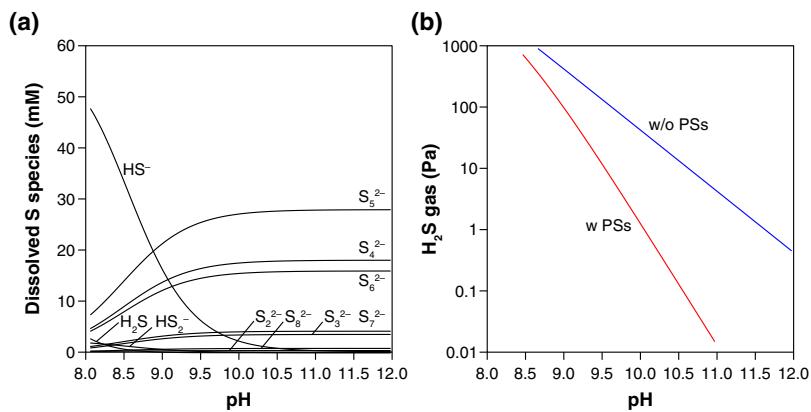
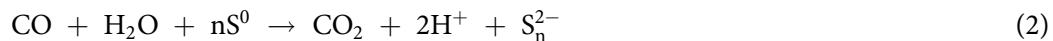



Figure 2 Thermodynamic prediction for the equilibrium concentrations of dissolved sulfur species (A) and gas-phase H_2S (B) after the urea synthesis reaction. In these calculations, the presence of an excess amount of S^0 for a complete conversion of CO (0.33 mmol) to urea or CO_2 was assumed (*i.e.*, the initial S^0/CO molar ratio ≫ 5; see the section "Thermodynamic calculation"). The blue line in (B) was calculated excluding PSs from the system. All the calculations were preformed using the experimentally derived thermodynamic data for PSs, HS⁻, H_2S reported in the literature (*Shock et al., 1997*; *Shock, Helgeson & Sverjensky, 1989*; *Robie & Hemingway, 1995*; *Kamyshny et al., 2004*, *2007*).

The amount of S^0 always decreased throughout the reaction; few or no S^0 remained in the experiments with the initial S^0/CO molar ratio less than 4.8 (Fig. S6). Meanwhile, the aqueous solutions exhibited a yellow color characteristic of PSs (*Bedoya-Lora, Hankin & Kelsall, 2019*); darker yellow was observed when larger amount of S^0 was used (Fig. S6). These features indicate that S^0 was reduced to PSs coupling with CO oxidation to urea (Eq. (1)) and CO_2 (Eq. (2))

$$CO + 2NH_3 + nS^0 \rightarrow (NH_2)_2CO + 2H^+ + S_n^{2-} \qquad (1)$$

$$CO + H_2O + nS^0 \rightarrow CO_2 + 2H^+ + S_n^{2-} \qquad (2)$$

Indeed, the molar amount of PSs formed through the reaction exhibited a one-to-one correlation with the amount of CO consumed (Fig. S7).

Thermodynamic calculation

Thermodynamic calculation predicts that in the presence of S^0, PSs are the dominant dissolved S species over HS⁻ and H_2S at the examined pH (10.3–10.5) (Fig. 2A). The presence of PSs with S^0 thus suppress the accumulation of H_2S by-product in the gas phase, keeping the H_2S gas concentration below 0.5 Pa in our experimental setting (Fig. 2B). When no PS formation was assumed, two orders of magnitude higher values (13–21 Pa) were calculated for the steady-state H_2S gas concentration after the complete conversion of CO to urea or CO_2 (Fig. 2B). Because the mean chain length of PSs is 5.0 (*i.e.*, $n = 5$ in S_n^{2-}, Fig. 2A), the capability of PSs to suppress H_2S accumulation is expected to work effectively at S^0/CO molar ratios higher than five. When an insufficient amount of S^0 is used (*e.g.*, S^0/CO molar ratio = 2), in contrast, the S^0-to-PSs reduction cannot fully extract the reduced sulfur ($S^0 \rightarrow S^{2-}$), resulting in an elevated emission of H_2S gas (Fig. 1B).

Thermodynamic calculations taking PSs into account thus explain our experimental results for H_2S. At the reaction temperatures of 35 °C, 50 °C, and 65 °C, the gas-phase H_2S are expected to reach 0.3–0.8, 1.4–3.0, and 4.7–9.8 Pa, respectively.

Based on the thermodynamic calculation (Fig. 2A), the urea synthesis reaction can be simplified as:

$$CO + 2NH_3 + 5S^0 \rightarrow (NH_2)_2CO + 2H^+ + S_5^{2-}$$ (3)

On average, five atoms of S^0 were converted to a single molecule of S_5^{2-} when one molecule of CO was consumed to form urea.

Kinetic characteristics

In water, PSs readily react with CO to form OCS (*Kamyshny et al., 2003*), a likely key intermediate in PS-assisted urea synthesis (Scheme 1). OCS was indeed observed in our experiments as a trace and transient gas species (Fig. S8). The formation rate of OCS is linearly proportional to the concentrations of CO and PSs (*Kamyshny et al., 2003*). Once formed, the OCS-to-urea conversion proceeds in competition with the OCS hydrolysis to CO_2, whose half-life is in the seconds-to-minutes range under the examined reaction conditions (*e.g.*, 18 s at pH10.0 and 50 °C; *Kamyshny et al., 2003*). Because CO_2 was a minor product in our experiments although the rate of OCS hydrolysis is much higher than that observed for urea synthesis (Fig. 1A), OCS formation is expected to be the rate-determining step of the overall urea synthesis process.

In accordance with this kinetic consideration, the experimental results (Fig. 1A), together with the corresponding CO consumption, were well represented with the following second-order rate equation parameterizing the CO and PS concentrations (Figs. 3A–3C):

$$\frac{d[\text{urea}]}{dt} = k[PSs][CO]$$ (4)

where [x] denotes the concentration of species x in water. Note that the urea-formation reaction (Eq. (1)) generates an equimolar amount of PSs while consuming an equimolar amount of CO. PSs and CO thus has the following kinetic relationships with urea in this reaction:

$$\frac{d[PSs]}{dt} = \frac{d[\text{urea}]}{dt}$$ (5)

$$\frac{d[CO]_{Tot}}{dt} = -V_L \frac{d[\text{urea}]}{dt}$$ (6)

In Eq. (6), the time derivative of the total amount of CO ($[CO]_{Tot}$) is correlated with that of urea concentration multiplied by the volume of sample solution (V_L), because CO is distributed in both the gas and aqueous phases. Thus, as long as competing reactions (*e.g.*, Eq. (2)) are not significant, CO and PSs do not need to be monitored during the experiment for the use of Eq. (4). Considering the high OCS hydrolysis rate at high pH (*Kamyshny et al., 2003*), a moderately alkaline pH (*e.g.*, pH 10–11) is preferable for such

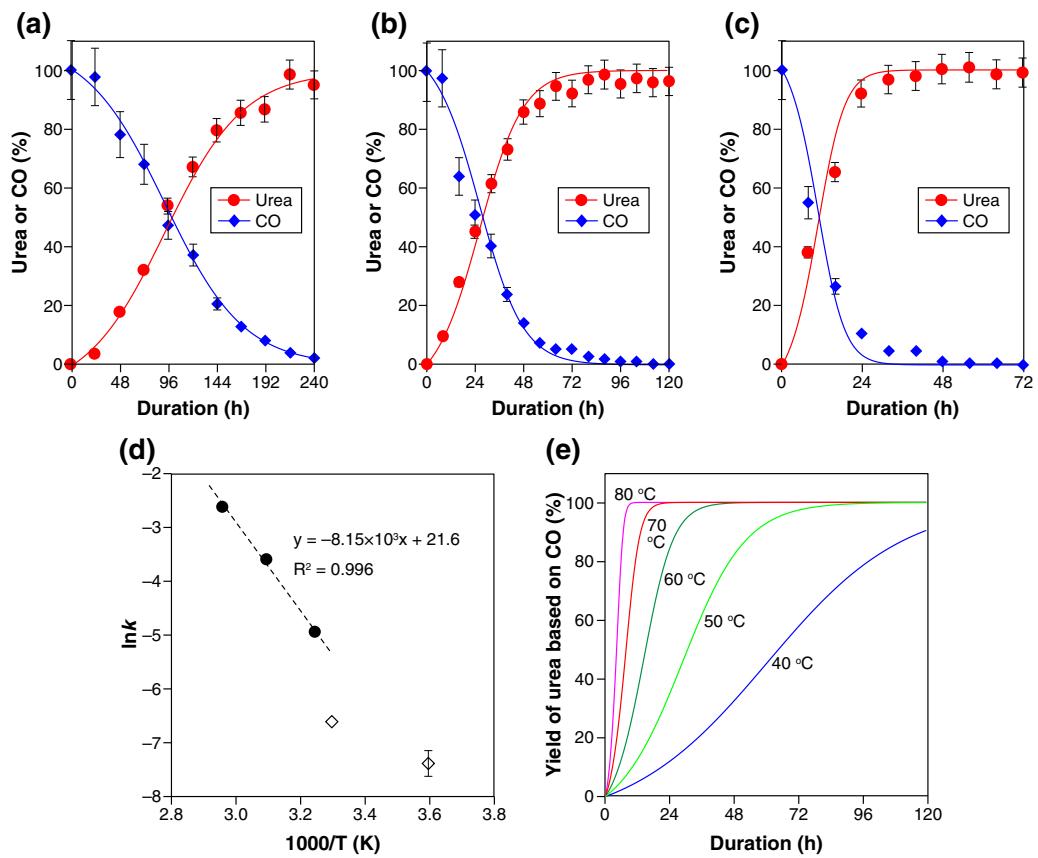



Figure 3 Kinetic characteristics of the polysulfide-assisted urea synthesis. (A–C) The experimental data (closed symbols) and fitted results (solid lines) for the CO-to-urea conversion at 35 °C (A), 50 °C (B), and 60 °C (C). The lines were calculated with Eqs. (4)–(6) by setting the rate constant k to 0.0072 (A), 0.028 (B), or 0.075 (C) mol^{-1} L^{-1} s^{-1}. The experimental data for urea are also shown in Fig. 1A. (D) Arrhenius plot of the obtained rate constants (closed circles). The reported rate constants for OCS formation from CO and PSs (*Kamyshny et al., 2003*) are also shown (open diamond symbols). (E) The yield of urea as a function of time between 40 °C and 80 °C calculated with the activation energy (Ea = 67.8 kJ mol^{-1}) and pre-exponential factor (ln(A) = 21.6) obtained from the Arrhenius plot (D).

selective urea synthesis. It is also suggested from the adequate kinetic representation (Figs. 3A–3C) that the other intermediate species (*i.e.*, thiocarbamate and isocyanate; Scheme 1) occupy a tiny fraction of the carbon compounds present in the course of the reaction.

Equations (4)–(6) also enabled us to reproduce the experimental results obtained without NaHS as the starting material (Fig. S9). However, this simulation requires the initial PS concentration to be a non-zero value (0.18 mM; see the caption of Fig. S9 for the other parameters). This low PS concentration is likely derived from the hydrolysis of S^0 ($4S^0 + 4H_2O \rightarrow 3HS^- + SO_4^{2-} + 5H^+$) (*Ellis & Giggenbach, 1971*) followed by the formation of PSs from S^0 and HS$^-$ (($n-1$)S^0 + HS$^-$ → S$_n^{2-}$ + H$^+$).

The determined rate constants k at three reaction temperatures (35 °C, 50 °C, and 65 °C) exhibited a linear trend in the Arrhenius plot (Fig. 3D). Extrapolation of the regression line to lower temperatures led to values roughly consistent with the reported

rate constants for OCS formation from CO and PSs (diamond symbols in Fig. 3D) (*Kamyshny et al., 2003*).

The activation energy (Ea = 67.8 kJ mol^{-1}) and pre-exponential factor (ln(A) = 21.6) obtained from the Arrhenius plot (Fig. 3D) enables us to predict the urea yield as a function of time in a range of temperature. For example, 80% yield of urea is calculated to be achieved within 98, 47, 23, 12, and 6 h at 40 °C, 50 °C, 60 °C, 70 °C, and 80 °C, respectively (Fig. 3E). Such estimations, together with the thermodynamic calculation for H$_2$S exemplified above, should be an important basis for realizing urea manufacturing with maximum productivity while minimizing the emission of H$_2$S gas.

Versatility of the PS-assisted reaction mechanism

Several techniques are available for the isolation and purification of urea from aqueous solution, such as forward osmosis (*Ray, Perreault & Boyer, 2019*), the use of adsorbents (*e.g.*, activated carbons, zeolites, ion-exchange resins, and silica) (*Urbanczyk, Sowa & Simka, 2016*), and selective dissolution in certain solvents (*e.g.*, ethanol) and subsequent recrystallization (*Marepula, Courtney & Randall, 2021*). Methods have also been developed for NH$_3$ recovery from wastewaters (*Kuntke et al., 2018*; *Kim, Moreno-Jimenez & Efstathiadis, 2021*). PSs is oxidized by O$_2$ to S^0 (*Steudel, Holdt & Nagorka, 1986*; *Kleinjan, de Keizer & Janssen, 2005*), which may be used for the next round of urea production. Urea can be isolated from dissolved inorganic species by utilizing its higher solubility in organic solvents (*Marepula, Courtney & Randall, 2021*). When ethanol is considered as a solvent for urea isolation from our product solution, the optimum purity of 88.2 mol% is expected based on the reported solubility data of urea and ammonium, sodium, and sulfate salts (*Lee & Lahti, 1972*; *Toro, Dobrosz-Gomez & Garcia, 2014*; *Galvao et al., 2021*). Experimental test of the isolation process and its further development must be a crucial next step for urea commercialization. It is also noteworthy that in addition to urea, NH$_3$, S^0, and SO$_4^{2-}$ (a by-product of PS oxidation) are well-used fertilizer components. Thus, not only as an isolated form, urea as a mixture component with the other N and S species could also be useful in agriculture (*Wagenfeld et al., 2019*).

The versatility of sulfur in water demonstrated in this study should also be beneficial to the production of various urea derivatives serving as intermediates for fine chemicals, pharmaceuticals, cosmetics and pesticides (*Franz & Applegath, 1961*; *Franz et al., 1961a*, *1961b*; *Mizuno et al., 2006*, *2007*; *Mizuno, Nakai & Mihara, 2009*; *Peng, Li & Xia, 2006*); thus, possessing wide applicability in material manufacturing. The reaction mechanism may also have played a role in prebiotic chemical processes in primordial hydrothermal vent environments rich in sulfur, CO and NH$_3$ that eventually led to the origin of life (*Li et al., 2017*; *Li, Kitadai & Nakamura, 2018*; *Nakashima et al., 2018*; *Lee et al., 2021*; *Kitadai, Kameya & Fujishima, 2017*; *Kitadai et al., 2018*, *2019*, *2021*).

CONCLUSIONS

In summary, we have reported selective CO conversion to urea in a mild aqueous ammonia solution assisted by PSs, and elucidated the thermodynamic and kinetic characteristics of this reaction. This simple and environmentally benign aqueous process

should be worth considering as a green and sustainable application of sulfur that is beneficial to agricultural activity.

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Competing Interests

The authors declare that they have no competing interests.

Author Contributions

- Norio Kitadai conceived and designed the experiments, performed the experiments, analyzed the data, prepared figures and/or tables, authored or reviewed drafts of the article, and approved the final draft.
- Satoshi Okada analyzed the data, authored or reviewed drafts of the article, dr. S. Okada considered the reaction mechanism, and approved the final draft.
- Akiko Makabe analyzed the data, authored or reviewed drafts of the article, dr. A. Makabe supported the product analysis, and approved the final draft.
- Eiji Tasumi analyzed the data, authored or reviewed drafts of the article, dr. E. Tasumi supported the product analysis, and approved the final draft.
- Masayuki Miyazaki analyzed the data, authored or reviewed drafts of the article, dr. M. Miyazaki supported the product analysis, and approved the final draft.

Data Availability

 The raw data are available in the Supplemental Files.

Supplemental Information

Supplemental information for this article can be found online at http://dx.doi.org/10.7717/peerj-ochem.6#supplemental-information.

REFERENCES

Ahmad N, Ahmad F, Khan I, Khan AD. 2015. Studies on the oxidative removal of sodium thiosulfate from aqueous solution. *Arabian Journal of Science and Engineering* **40(2)**:289–293 DOI 10.1007/s13369-014-1473-0.

Avetisyan K, Buchshtav T, Kamyshny A Jr. 2019. Kinetics and mechanism of polysulfides formation by a reaction between hydrogen sulfide and orthorhombic cyclooctasulfur. *Geochimica et Cosmochimica Acta* **247**:96–105 DOI 10.1016/j.gca.2018.12.030.

Bargiacchi E, Antonelli M, Desideri U. 2019. A comparative assessment of Power-to-Fuel production pathways. *Energy* **183**:1253–1265 DOI 10.1016/j.energy.2019.06.149.

Bedoya-Lora FE, Hankin A, Kelsall GH. 2019. In situ determination of polysulfides in alkaline hydrogen sulfide solutions. *Electrochimica Acta* **314**:40–48 DOI 10.1016/j.electacta.2019.04.119.

Bodirsky BL, Popp A, Lotze-Campen H, Dietrich JP, Rolinski S, Weindl I, Schmitz C, Muller C, Bonsch M, Humpenoder F, Biewald A, Stevanovic M. 2014. Reactive nitrogen requirements to feed the world in 2050 and potential to mitigate nitrogen pollution. *Nature Communions* **5(1)**:3858 DOI 10.1038/ncomms4858.

Diaz DJ, Darko AK, McElwee-White L. 2007. Transition metal-catalyzed oxidative carbonylation of amines to ureas. *European Journal of Organic Chemistry* **2007(27)**:4453–4465 DOI 10.1002/ejoc.200700148.

Ellis AJ, Giggenbach W. 1971. Hydrogen sulphide ionization and sulphur hydrolysis in high temperature solution. *Geochimica et Cosmochimica Acta* **35(3)**:247–260 DOI 10.1016/0016-7037(71)90036-6.

Erisman JW, Sutton MA, Galloway J, Klimont Z, Winiwarter W. 2008. How a century of ammonia synthesis changed the world. *Nature Geoscience* **1(10)**:636–638 DOI 10.1038/ngeo325.

Franz RA, Applegath F. 1961. A new urea synthesis. I. The reaction of ammonia, carbon monoxide, and sulfur. *Journal of Organic Chemistry* **26(9)**:3304–3305 DOI 10.1021/jo01067a065.

Franz RA, Applegath F, Morriss FV, Baiocchi F. 1961a. A new synthesis of ureas. II. The reaction of primary aliphatic amines with carbon monoxide and sulphur. *Journal of Organic Chemistry* **26(9)**:3306–3308 DOI 10.1021/jo01067a066.

Franz RA, Applegath F, Morriss FV, Baiocchi F, Bolze C. 1961b. A new synthesis of ureas. III. The reaction of aromatic amines with carbon monoxide and sulfur. *Journal of Organic Chemistry* **26**:3309–3312 DOI 10.1021/jo01067a067.

Fuentes-Lara LO, Medrano-Macias J, Perez-Labrada F, Rivas-Martinez EN, Garcia-Enciso EL, Gonzalez-Morales S, Juarez-Maldonado A, Rincon-Sanchez F, Benavides-Mendoza A. 2019. From elemental sulfur to hydrogen sulfide in agricultural soils and plants. *Molecules* **24**:2282 DOI 10.3390/molecules24122282.

Fukuto JM, Ignarro LJ, Nagy P, Wink DA, Kevil CG, Feelisch M, Cortese-Krott MM, Bianco CL, Kumagai Y, Hobbs AJ, Lin J, Ida T, Akaike T. 2018. Biological hydropersulfides and related polysulfides–a new concept and perspective in redox biology. *FEBS Letters* **592**:2140–2152 DOI 10.1002/1873-3468.13090.

Galvao AC, Jimenez YP, Justel FJ, Robazza WS, Feyh JVT. 2021. Modeling of the solid-liquid equilibrium of NaCl, KCl and NH4Cl in mixtures of water and ethanol by the modified Pitzer model. *Journal of Molecular Liquids* **322**:114968 DOI 10.1016/j.molliq.2020.114968.

Giddey S, Badwal SPS, Kulkarni A. 2013. Review of electrochemical ammonia production technologies and materials. *International Journal of Hydrogen Energy* **38**:14576–14594 DOI 10.1016/j.ijhydene.2013.09.054.

Glibert PM, Harrison J, Heil C, Seitzinger S. 2006. Escalating worldwide use of urea–a global change contributing to coastal eutrophication. *Biogeochemistry* **77**:441–463 DOI 10.1007/s10533-005-3070-5.

Griffith CM, Woodrow JE, Seiber JN. 2015. Environmental behaviour and analysis of agricultural sulfur. *Pest Management Science* **71(11)**:1486–1496 DOI 10.1002/ps.4067.

Huber C, Wachtershauser G. 1998. Peptides by activation of amino acids with CO on (Ni,Fe)S surfaces: Implications for the origin of life. *Science* **281(5377)**:670–672 DOI 10.1126/science.281.5377.670.

Kamyshny A Jr, Goifman A, Rizkov D, Lev O. 2003. Formation of carbonyl sulfide by the reaction of carbon monoxide and inorganic polysulfides. *Environmental Science & Technology* **37(9)**:1865–1872 DOI 10.1021/es0201911.

Kamyshny A Jr, Goifman A, Gun J, Rizkov D, Lev O. 2004. Equilibrium distribution of polysulfide ions in aqueous solutions at 25 °C: a new approach for the study of polysulfides equilibria. *Environmental Science & Technology* **38(24)**:6633–6644 DOI 10.1021/es049514e.

Kamyshny A Jr, Gun J, Rizkov D, Voitsekovski T, Lev O. 2007. Equilibrium distribution of polysulfide ions in aqueous solutions at different temperatures by rapid single phase derivatization. *Environmental Science & Technology* **41**:2395–2400 DOI 10.1021/es062637+.

Kim KY, Moreno-Jimenez DA, Efstathiadis H. 2021. Electrochemical ammonia recovery from anaerobic centrate using a nickel-functionalized activated carbon membrane electrode. *Environmental Science & Technology* **55**:7674–7680 DOI 10.1021/acs.est.1c01703.

Kitadai N, Kameya M, Fujishima K. 2017. Origin of the reductive tricarboxylic acid (rTCA) cycle-type CO_2 fixation: a perspective. *Life* **7**:39 DOI 10.3390/life7040039.

Kitadai N, Nakamura R, Yamamoto M, Takai K, Li Y, Yamaguchi A, Gilbert A, Ueno Y, Yoshida N, Oono Y. 2018. Geoelectrochemical CO production: implications for the autotrophic origin of life. *Science Advances* **4**:eaao7265 DOI 10.1126/sciadv.aao7265.

Kitadai N, Nakamura R, Yamamoto M, Takai K, Yoshida N, Oono Y. 2019. Metals likely promoted protometabolism in early ocean alkaline hydrothermal systems. *Science Advances* **5**:eaav7848 DOI 10.1126/sciadv.aav7848.

Kitadai N, Nakamura R, Yamamoto M, Okada S, Takahagi W, Nakano Y, Takahashi Y, Takai K, Oono Y. 2021. Thioester synthesis through geoelectrochemical CO_2 fixation on Ni sulfides. *Communications Chemistry* **4**:37 DOI 10.1038/s42004-021-00475-5.

Kleinjan WE, de Keizer A, Janssen AJH. 2005. Kinetics of the chemical oxidation of polysulfide anions in aqueous solution. *Water Research* **39**:4093–4100 DOI 10.1016/j.watres.2005.08.006.

Kuntke P, Rodrigues M, Sleutels T, Saakes M, Hamelers HVM, Buisman CJN. 2018. Energy-efficient ammonia recovery in an up-scaled hydrogen gas recycling electrochemical system. *ACS Sustainable Chemistry & Engineering* **6**:7638–7644 DOI 10.1021/acssuschemeng.8b00457.

Lara JMG, Cardona FP, Vallmajor AR, Cadevall MC. 2019. Oxidation of thiosulfate with oxygen using copper (II) as a catalyst. *Metals* **9**:387 DOI 10.3390/met9040387.

Lee FM, Lahti LE. 1972. Solubility of urea in water-alcohol mixtures. *Journal of Chemical and Engineering Data* **17**:304–306 DOI 10.1021/je60054a020.

Lee JE, Yamaguchi A, Ooka H, Kazumi T, Miyauchi M, Kitadai N, Nakamura R. 2021. *In situ* FTIR study of CO_2 reduction on inorganic analogues of carbon monoxide dehydrogenase. *Chemical Communications* **57**:3267–3270 DOI 10.1039/D0CC07318K.

Leman L, Orgel L, Ghadiri MR. 2004. Carbonyl sulfide-mediated prebiotic formation of peptides. *Science* **306**:283–286 DOI 10.1126/science.1102722.

Leman LJ, Orgel LE, Ghadiri MR. 2006. Amino acid dependent formation of phosphate anhydrides in water mediated by carbonyl sulfide. *Journal of American Chemical Society* **128**:20–21 DOI 10.1021/ja056036e.

Li Y, Yamaguchi A, Yamamoto M, Takai K, Nakamura R. 2017. Molybdenum sulfide: a bioinspired electrocatalyst for dissimilatory ammonia synthesis with geoelectrical current. *Journal of Physical Chemistry C* **121**:2154–2164 DOI 10.1021/acs.jpcc.6b08343.

Li Y, Kitadai N, Nakamura R. 2018. Chemical diversity of metal sulfide minerals and its implications for the origin of life. *Life* **8**:46 DOI 10.3390/life8040046.

Lucheta AR, Lambais MR. 2012. Sulfur in agriculture. *Revista Brasileira De Ciencia Do Solo* **36(5)**:1369–1379 DOI 10.1590/S0100-06832012000500001.

Marepula H, Courtney CE, Randall DG. 2021. Urea recovery from stabilized urine using a novel ethanol evaporation and recrystallization process. *Chemical Engineering Journal Advances* **8**:100174 DOI 10.1016/j.ceja.2021.100174.

Mizuno T, Iwai T, Ishino Y. 2005. Solvent-assisted thiocarboxylation of amines and alcohols with carbon monoxide and sulfur under mild conditions. *Tetrahedron* **61(38)**:9157–9163 DOI 10.1016/j.tet.2005.06.114.

Mizuno T, Mihara M, Iwai T, Ito T, Ishino Y. 2006. Practical synthesis of urea derivatives from primary amines, carbon monoxide, sulfur, and oxygen under mild conditions. *Synthesis* **17(17)**:2825–2830 DOI 10.1055/s-2006-942491.

Mizuno T, Mihara M, Nakai T, Iwai T, Ito T. 2007. Solvent-free synthesis of urea derivatives from primary Amines and sulfur under carbon monoxide and oxygen at atmospheric pressure. *Synthesis* **20**:3135–3140 DOI 10.1055/s-2007-990793.

Mizuno T, Nakai T, Mihara M. 2009. Synthesis of unsymmetrical ureas by sulfur-assisted carbonylation with carbon monoxide and oxidation with molecular oxygen under mild conditions. *Synthesis* **15**:2492–2496 DOI 10.1055/s-0029-1216863.

Nakashima S, Kebukawa Y, Kitadai N, Igisu M, Matsuoka N. 2018. Geochemistry and the origin of life: from extraterrestrial processes, chemical evolution on Earth, fossilized life's records, to natures of the extant life. *Life* **8**:39 DOI 10.3390/life8040039.

Naz MY, Sulaiman SA. 2016. Slow release coating remedy for nitrogen loss from conventional urea: a review. *Journal of Controlled Release* **225**:109–120 DOI 10.1016/j.jconrel.2016.01.037.

Peng XG, Li FW, Xia CG. 2006. A highly efficient sulfur-catalyzed oxidative carbonylation of primary amines and beta-amino alcohols. *Synlett* **8**:1161–1164 DOI 10.1055/s-2006-926254.

Rafiee A, Khalilpour KR, Milani D, Panahi M. 2018. Trends in CO_2 conversion and utilization: a review from process systems perspective. *Journal of Environmental Chemical Engineering* **6**:5771–5794 DOI 10.1016/j.jece.2018.08.065.

Rappold TA, Lackner KS. 2010. Large scale disposal of waste sulfur: from sulfide fuels to sulfate sequestration. *Energy* **35(3)**:1368–1380 DOI 10.1016/j.energy.2009.11.022.

Ray H, Perreault F, Boyer TH. 2019. Urea recovery from fresh human urine by forward osmosis and membrane distillation (FO-MD). *Environmental Science Water Research & Technology* **5(11)**:1993–2003 DOI 10.1039/C9EW00720B.

Roig A, Cayuela ML, Sanchez-Monedero MA. 2004. The use of elemental sulphur as organic alternative to control pH during composting of olive mill wastes. *Chemosphere* **57(9)**:1099–1105 DOI 10.1016/j.chemosphere.2004.08.024.

Robie RA, Hemingway BS. 1995. *Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 bar (10^5 Pascals) Pressure and at Higher Temperatures.* U.S. Geological Survey Bulletin 2131, U.S. Geological Survey. *Available at https://pubs.er.usgs.gov/publication/b2131.*

Sahu SK, Ajmal PY, Bhangare RC, Tiwari M, Pandit GG. 2014. Natural radioactivity assessment of a phosphate fertilizer plant area. *Journal of Radiation Research and Applied Sciences* **7(1)**:123–128 DOI 10.1016/j.jrras.2014.01.001.

Saleh TA. 2020. Characterization, determination and elimination technologies for sulfur from petroleum: Toward cleaner fuel and a safe environment. *Trends in Environmental Analytical Chemistry* **25**:e00080 DOI 10.1016/j.teac.2020.e00080.

Satanowski A, Bar-Even A. 2020. A one-carbon path for fixing CO_2. *EMBO reports* **21**:e50273 DOI 10.15252/embr.202050273.

Smith C, Hill AK, Torrente-Murciano L. 2020. Current and future role of Haber-Bosch ammonia in a carbon-free energy landscape. *Energy & Environmental Science* **13**:331–344 DOI 10.1039/c9ee02873k.

Shock EL, Helgeson HC, Sverjensky DA. 1989. Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of inorganic neutral species. *Geochimica et Cosmochimica Acta* **53**:2157–2183 DOI 10.1016/0016-7037(90)90429-O.

Shock EL, Sassani DC, Willis M, Sverjensky DA. 1997. Inorganic species in geologic fluids: correlations among standard molal thermodynamic properties of aqueous ions and hydroxide complex. *Geochimica et Cosmochimica Acta* **61**:907–950 DOI 10.1016/S0016-7037(96)00339-0.

Srivastava VC. 2012. An evaluation of desulfurization technologies for sulfur removal from liquid fuels. *RSC Advances* **2**:759–783 DOI 10.1039/C1RA00309G.

Steudel R, Holdt G, Nagorka R. 1986. On the autoxidation of aqueous sodium polysulfide. *Zeitschrift Fur Naturforschung Section B-A Journal of Chemical Sciences* **41(12)**:1519–1522 DOI 10.1515/znb-1986-1208.

Tiu BDB, Advincula RC. 2015. Polymeric corrosion inhibitors for the oil and gas industry: Design principles and mechanism. *Reactive and Functional Polymers* **95**:25–45 DOI 10.1016/j.reactfunctpolym.2015.08.006.

Toro JCO, Dobrosz-Gomez I, Garcia MAG. 2014. Sodium sulfate solubility in (water + ethanol) mixed solvents in the presence of hydrochloric acid: experimental measurements and modeling. *Fluid Phase Equilibria* **384**:106–113 DOI 10.1016/j.fluid.2014.10.025.

Urbanczyk E, Sowa M, Simka W. 2016. Urea removal from aqueous solutions-a review. *Journal of Applied Electrochemistry* **46(10)**:1011–1029 DOI 10.1007/s10800-016-0993-6.

Wagenfeld JG, Al-Ali K, Almheiri S, Slavens AF, Calvet N. 2019. Sustainable applications utilizing sulfur, a by-product from oil and gas industry: a state-of-the-art review. *Waste Management* **95**:78–89 DOI 10.1016/j.wasman.2019.06.002.

Wesolowska M, Rymarczyk J, Gora R, Baranowski P, Slawinski C, Klimczyk M, Supryn G, Schimmelpfennig L. 2021. New slow-release fertilizers–economic, legal and practical aspects: a review. *International Agrophysics* **35(1)**:11–24 DOI 10.31545/intagr/131184.

Zendehboudi S, Zahedi G, Bahadori A, Lohi A, Elkamel A, Chatzis I. 2014. A dual approach for modelling and optimisation of industrial urea reactor: smart technique and grey box model. *Canadian Journal of Chemical Engineering* **92(3)**:469–485 DOI 10.1002/cjce.21824.