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# Elucidating the Reaction Mechanisms between Triazine and Hydrogen Sulfide with pH Variation Using Mass Spectrometry

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ABSTRACT: Triazine is one of the most economical and effective scavengers for hydrogen sulfide (H<sub>2</sub>S) removal, but the reaction

mechanisms between triazine and  $H_2S$  with pH variation in solution are still poorly understood. Herein we show that the reaction process can be directly probed by means of paper spray mass spectrometry, in which an aprotic solvent (e.g., acetonitrile) is more favorable to the observation of reaction intermediates than a protic solvent (e.g., methanol) owing to hydrogen bond interaction. Varying the pH of the reaction leads to completely different reaction pathways. With the pH in the range of 5.58 to 7.73,



the major product was thiadiazine. With a pH to 3.02 - 3.69, thiadiazine is converted into 2-(5-(2-hydroxyethyl)-1,3,5-thiadiazinan-3-yl)acetaldehyde, which differs from the traditional pathway of analogous reactions. However, as ammonia was added into the reaction and the pH was adjusted to the range 8.45 - 9.43, triazine readily undergoes hydrolysis, and the formed intermediate reacts with ammonia and formaldehyde generated *in situ* from triazine to produce 1-(2-hydroxyethyl)-3,5,7-triaza-1-azoniatricyclo [3.3.1.1<sup>3,7</sup>]decane (HTAD). Further increasing the pH up to 10.27 - 11.21 leads to the decomposition of HTAD. Based on the experimental observation and evidences from high resolution and tandem mass spectrometry, we propose the plausible reaction mechanisms between triazine and H<sub>2</sub>S as well as the derived reaction from triazine under different pH conditions.

### 1. INTRODUCTION

In the exploitation and production of oil and gas, hydrogen sulfide (H<sub>2</sub>S) is a commonly encountered pollutant, and its removal is of prime importance due to health, environmental and corrosion issues. Several techniques, including adsorption and membrane separation,<sup>1-3</sup> have been developed to eliminate H<sub>2</sub>S during processing. As H<sub>2</sub>S concentration is typically below a few hundred parts per million (ppm), the most economical and effective solution is the non-regenerative one, and an economically affordable and fast rate of reaction makes aqueous soluble 1,3,5-tris(2-hydroxyethyl)hexahydros-triazine (later called triazine) one of the most attractive option, which could reduce H<sub>2</sub>S concentrations down to around 5 ppm in streams.<sup>3</sup> In spite of this, the optimal conditions for H<sub>2</sub>S removal are not always applied because the reaction details are not well known. To gain insight into the reaction, various techniques, including X-ray diffraction, elemental analysis and NMR analysis,<sup>4-7</sup> field asymmetric ion mobility spectrometry<sup>8</sup> and gas chromatography-mass spectrometry,<sup>9</sup> have been employed. The currently accepted

pathway for the reaction between triazine and  $H_2S$  is depicted in **Figure 1a**.<sup>1,3,6,7,10</sup> Triazine first reacts with  $H_2S$  by the generation of 3,5-di-(2-hydroxyethyl)-hexahydro-1,3,5-thiadiazine (thiadiazine), where a nitrogen atom is substituted with a sulfur atom. The resulting thiadiazine then reacts with  $H_2S$ 



**Figure 1. (a)** Reaction between triazine and  $H_2S$  forming thiadiazine, dithiazine and trithiane; **(b)** Schematic representation of the procedure for analyzing the reaction solution using paper spray mass spectrometry.

forming 5-(2-hydroxyethyl)-hexa-hydro-1,3,5-dithiazine (dithiazine), which further interacts with  $H_2S$ , finally producing strithiane (trithiane). However, the effectiveness of triazine on  $H_2S$  removal is strongly dependent on temperature, pH, contact time, and natural gas composition.<sup>11,12</sup> Among them, the pH value of oil and gas fields varies significantly with the depth of the well.<sup>13</sup> This would have a great effect on triazine reactivity with  $H_2S$  because the hydrolysis rate of triazine is strongly dependent on the pH of the reaction solution.<sup>7</sup> However, the reaction mechanisms between triazine and  $H_2S$  under various pH values are still poorly understood.

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Mass spectrometry has been demonstrated to be a powerful technique for chemical analysis based on its sensitivity, specificity, and precision. The development of ambient ionization simplifies this technique by eliminating sample pretreatment prior to the final analysis.<sup>14</sup> This greatly facilities application of MS analysis to reaction monitoring and mechanism determination.<sup>15-20</sup> In the case of the reaction between triazine and H<sub>2</sub>S, some attempts have been made to elucidate the reaction mechanism using mass spectrometry. Madsen et al.<sup>10,21</sup> investigated the reaction products and their fragmentation products from triazine and H<sub>2</sub>S using electrospray ionization mass spectrometry (ESI-MS), and possible pathways and structures were suggested to describe the observed products. They also studied the precipitate by use of triazines for H<sub>2</sub>S scavenging, and found the generated polymer, result-

ing from the decomposition of dithiazine to methanedithiol followed by reacting between dithiazine and other methanedithiol molecules, had an empirical formula of  $(C_7H_{15}S_{4.5}NO)_n$  after identification by ESI-MS in tandem with infrared spectroscopy and X-ray diffraction.<sup>5</sup> Those investigations are of significance to better understand the reaction pathway and additional products<sup>10,21</sup> as well as the fouling formation<sup>5</sup> involved in H<sub>2</sub>S scavenging with triazine.

Herein, we use paper spray mass spectrometry (PS-MS),<sup>22</sup> owing to its unique features (e.g., simplicity, low-cost and without sample pretreatment) and success in chemical reactivity assessment,<sup>23-28</sup> to characterize the reaction mechanisms between triazine and  $H_2S$  as a function of the pH of the reaction solution. Evidences from experimental observations using high resolution and tandem mass spectrometry identify the ionic species involved in the reaction procedures, and plausible mechanisms are proposed to elucidate the complex reaction inside the process.

#### 2. RESULTS AND DISCUSSION

**3.1 Selection of reaction solvent.** To detect the ionic and/or ionizable species in the reaction between triazine and H<sub>2</sub>S, paper spray mass spectrometry (PS-MS)<sup>22</sup> was employed as shown in **Figure 1b**, in which 25  $\mu$ L reaction solution was directly dropped on a piece of triangle filter paper without any pretreatment followed by applying a +3.5 kV DC voltage to generate the spray and MS measurement. The current method contrasted with prior procedures that first dropped several microliters of sample solution on the paper substrate, dried the solution, and then applied solvent for paper spray.<sup>29,30</sup> In this way, a layer of reaction solution would be floating at the surface of the filter paper. Before the exhaustion of reaction solution in a spray event less than 1 min, the experiment would be complete. So the species in solution had less chance to contact the paper substrate and are readily eluted, similar to a previous report on analysis of protein complexes.<sup>31</sup> During the course of the reaction (see Experimental Section for details), the solvent was found to play a crucial role in determining the observed species. As protic solvents such as methanol were employed (Figure 2a), the dominant peaks were either the by-products of the scavenging reaction (m/z 62 and 86, Figures S1 and S2)<sup>10</sup> or the species derived from acetic acid (m/z 105, 165, 187, 197, 229 and 269). Under these conditions, it was difficult to observe the reaction products such as thiadiazine (m/z 193) and trithiane (m/z 139). Although a peak at m/z 166 was present (Figure 2a), further experiments based on tandem mass analysis and high resolution mass spectrometry (Figures S3 and **S4**) indicated that it was a mixture composed of  $C_4H_8O_4NS^+$ ,  $C_5H_{12}ONS_2^+$  (dithiazine) and  $C_4H_{10}O_3NNa^+$ . When aprotic solvents such as acetonitrile were used (Figure 2b), it was interesting to observe abundant reaction products, thiadiazine ([M+H]<sup>+</sup>, m/z 193 as **Figure 2c** and [M+Na]<sup>+</sup>, m/z 215), and additional species resulting from sodiated triazine adduct ([M+Na]<sup>+</sup>, m/z 242 as Figure 2d) and side reaction (m/z 62, 74, 86 and 120) (Figures S1 and S2) as well as the species derived



**Figure 2.** Mass spectra of the reaction between triazine and Na<sub>2</sub>S in the presence of 0.1% acetic acid using (a) methanol and (b) acetonitrile as solvents, respectively; MS/MS spectra of the species occurred at (c) m/z 242 and (d) m/z 193 by reaction between triazine and Na<sub>2</sub>S with a molar ratio of 1:1 in the presence of 0.1% HOAc in acetonitrile.

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from acetic acid (m/z 105, 187 and 269) and acetonitrile (m/z 146). Under those conditions, the product occurring at m/z 166 was absent. The results from different molar ratios between triazine and Na<sub>2</sub>S in the presence of 0.1% acetic acid (HOAc) suggest that this phenomenon could be ascribed to the lower amount of Na<sub>2</sub>S involved in the reaction (Figures S3). However, in both methanol and acetonitrile reaction systems, the reaction product, trithiane (m/z 139), was barely detectable, in agreement with the previous reports,<sup>6,7,10</sup> presumably due to the lower reactivity of dithiazine than triazine and thiadiazine towards the generated H<sub>2</sub>S.<sup>7</sup> More important-10 ly, the peak intensity of the reaction product, thiadiazine (m/z 11 193), in an aprotic solvent (e.g., acetonitrile) is much more 12 abundant than that in a protic solvent (e.g., methanol), and 13 similar results were obtained from other solvents (e.g., water, 14 ethanol, propanol, acetone, ethyl ether and ethyl acetate as 15 Figure S5). This reveals that an aprotic solvent is more favor-16 able to the observation of the reaction between triazine and 17 H<sub>2</sub>S than a protic solvent attributable to the strong hydrogen 18 bond interaction between the solvent used and the reactants 19 or products. Based on this observation, an aprotic solvent, 20 acetonitrile, was used to explore the reaction mechanisms 21 between triazine and  $H_2S$  at various pH values in reaction 22 solutions. 23

3.2 Effect of acidity on the reaction between triazine and H<sub>2</sub>S. As reported in the literature,<sup>7,11,12</sup> the pH of the reaction solution has a significant effect on the efficiency of H<sub>2</sub>S scavenging using triazine. To explore the effect of solution pH on the reaction between triazine and Na<sub>2</sub>S, we adjusted its acidity by using HOAc. With increase in the acidity of reaction solution, abundant and stable signals were obtained for all conditions (Figures 3 and S6), suggesting that the variation of pH had little effect on the ionization of paper spray. When there was no HOAc involved in the reaction (pH 9.49, Figure 3a), the dominant peaks in the mass spectrum were the sodiated triazine ([M+Na]<sup>+</sup>, m/z 242) and the hydrolyzed product of tria-

zine (m/z 74).<sup>7,10</sup> As 0.1% (v/v) HOAc was added into the reaction system (Figure 3b), the peak at m/z 193 became dominant, indicating the transformation of sodiated triazine (m/z 242) into thiadiazine (m/z 193). In addition, several peaks (m/z 62, 86, 120 and 218) resulting from the hydrolyzed triazine or  ${\sf thiadiazine}^{10}$ appeared besides the one at m/z 74. Further increasing the amount of HOAc from 0.1% to 1% led to the decrease in the total signal intensity, and species derived from HOAc (m/z 105, 187, 229 and 269) occurred besides those above (Figure 3c and d). When the amount of HOAc in the reaction system



Figure 3. Mass spectra of the solutions from the reaction between triazine and Na<sub>2</sub>S in the presence of different percentages of acetic acid: (a) 0% (v/v, pH 9.49), (b) 0.1% (v/v, pH 7.73), (c) 0.5% (v/v, pH 6.40), (d) 1% (v/v, pH 5.58), (e) 5% (v/v, pH 3.69) and (f) 10% (v/v, pH 3.02) using acetonitrile as solvent.

was above 5% (pH below than 3.69), the peak at m/z 193 was not the most dominant, and another peak at m/z 191 emerged and became dominant (Figure 3e). Furthermore, increasing the acidity in solution led to a gradually increased intensity of the peak at m/z 191, whereas the peak at m/z 193



Figure 4. (a) Variation in the peak intensity of the species at m/z 193, m/z 191 and m/z 218 with time from the reaction between triazine and  $Na_2S$  in the presence of 5% HOAc; MS/MS spectra of (b) m/z 218 and (c) 191 in 5% HOAc; and MS/MS spectra of m/z 193 in the presence of (d) 0.1%, (e) 1.0% and (f) 5.0% HOAc using acetonitrile as solvent.

became weaker (Figure 3f). These results demonstrate that the acidity in solution has a pronounced influence on the reaction of triazine and Na<sub>2</sub>S. When the pH was in the range of 5.58 - 7.73 (Figure 3b-d), thiadiazine (m/z 193) was the dominant reaction product. However, as the pH in solution was below 3.69 (Figure 3e and f), the species at m/z 191 overwhelmed the others. To determine the evolution of the peak at m/z 191, we systematically investigated its change in peak abundance with reaction time for the reaction system with 5% HOAc. As shown in Figure S7, with extension in the reaction time, the peak at m/z 193 initially increased, but then decreased, whereas the species at m/z 191 emerged after a reaction time of 10 min. Extending the reaction time led to its gradual increase in abundance until it became the dominant peak after 6 h. For reaction periods above 48 h, its intensity kept almost constant. Interestingly, a peak at m/z 218 behaved analogously to that at m/z 191 (Figures S6 and 4a). Further experiments indicated that the species at m/z 218 and 191 had compositions of  $C_9H_{20}O_3N_3^+$  and  $C_7H_{15}O_2N_2S^+$ (Figure S8), which were just 2H less than protonated triazine  $(m/z 220, C_9H_{22}O_3N_3^{\dagger})$  and thiadiazine  $(m/z 193, C_7H_{17}O_2N_2S^{\dagger})$ , respectively. Such dehydrogenation is a common phenomenon in the process of electron ionization, but is not expected in paper spray due to soft ionization. Based on the above discussion and the results from MS/MS spectra of m/z 218, 220, 191 and 193 (Figures 4b-d and S9), it could be speculated that the species at m/z 191 was derived from the reaction between the one at m/z 218 and  $H_2S$ , similar to thiadiazine (m/z 193) from the reaction of triazine (m/z 220) with  $H_2S$ (Figure 1a).

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29 We also observed that the composition of the species at 30 m/z 193 changed both with increase in the HOAc content in 31 the reaction solution (Figure 4d-f) and with extension in the 32 reaction time as the HOAc content was 5% (Figure S10). As 33 shown in their corresponding MS/MS spectra, there was a 34 tiny peak at m/z 145 steadily appeared and demonstrated an 35 increasing trend with variation in the experimental conditions, 36 and, more importantly, the peak intensity of m/z 120 gradual-37 ly became weaker under the same energy during the collision induced dissociation (CID, Figure S10). This suggested that the 38 composition of the species at m/z 193 varied with experi-39 mental conditions. The results from a high resolution Orbitrap 40 mass spectrometer (Figures S2d and d', S8c and c' and S11) 41 revealed that the species was a mixture of  $C_7H_{15}O_2N_2^{34}S^+$  (m/z 42 193.0805) and  $C_7H_{17}O_2N_2^{32}S^+$  (193.1004). More importantly, 43 with changes in the experimental conditions, the level of 44  $C_7H_{15}O_2N_2^{34}S^{+}$ progressively overwhelmed that of 45  $C_7H_{17}O_2N_2^{32}S^+$ . As discussed above, the latter had a structure 46 of 3,5-di-(2-hydroxyethyl)-hexahydro-1,3,5-thiadiazine, name-47 ly thiadiazine, which was the dominant reaction product be-48 tween triazine and H<sub>2</sub>S as the associated HOAc content was 49 below 1% (Figure 3b-d). Taking into account the sharp de-50 crease in the content of thiadiazine and the progressive in-51 crease in the levels of  $C_7H_{15}O_2N_2S^{\dagger}$  (m/z 191) and  $C_9H_{20}O_3N_3^{\dagger}$ 52 (m/z 218) as Figures 3, 4a and S7, the plausible reaction 53 mechanisms during H<sub>2</sub>S scavenging using triazine with varia-54 tion in solution acidity are proposed as Scheme 1. When the 55 pH of the reaction solution is in the range of 5.58 -9.49, tria-56 zine (I) will either directly react with H<sub>2</sub>S by production of 57 thiadiazine (II) or be first sodiated to form sodiated triazine 58



Scheme 1. Proposed Reaction Mechanisms between Triazine and  $H_2S$  with Variation in Solution Acidity.

(m/z 242) followed by reaction with  $H_2S$  to generate protonated thiadiazine (m/z 193). If the pH is decreased to the range of 3.02 to 3.69, there are two pathways leading to the conversion of the thiadiazine (II) or sodiated triazine (V, m/z



**Figure 5.** After the reaction between triazine and Na<sub>2</sub>S in the presence of 0.1% HOAc for 5 h, add different percentages of ammonia solution into the above solution followed by reaction for 30 min: (a) 0% (v/v, pH 7.73), (b) 0.1% (v/v, pH 8.45), (c) 0.5% (v/v, pH 8.91), (d) 1.0% (v/v, pH 9.43), (e) 5.0% (v/v, pH 10.27), (f) 10% (v/v, pH 10.60), (g) 15% (v/v, pH 11.01)and (h) 20% (v/v, pH 11.21) using acetonitrile as solvent (note: the concentration means the final value in the reaction solution).

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242) into protonated 2-(5-(2-hydroxyethyl)-1,3,5thiadiazinan-3-yl)acetaldehyde (IV, m/z 191). One pathway is that thiadiazine (II) first becomes sodiated thiadiazine (III, m/z 215) followed by loss of NaH with generation of IV. In another route, one molecule of NaH is first lost from sodiated triazine (V) by formation of protonated 2-(3,5-bis(2-hydroxyethyl)-1,3,5-triazinan-1-yl)acetaldehyde (VI, m/z 218). Then VI will further react with H<sub>2</sub>S by production of IV. In this process, the pH in solution plays a central role in determining the reaction pathway. At a higher pH, triazine is prone to become into thiadiazine (II, m/z 193). On the contrary, 2-(5-(2hydroxyethyl)-1,3,5-thiadiazinan-3-yl)acetaldehyde (IV, m/z 191) is the favorable product (Figure 3).

3.3 Effect of base on the reaction between triazine and H<sub>2</sub>S. These experiments were carried out by adding different amounts of ammonia into the solution after the reaction between triazine and Na<sub>2</sub>S in the presence of 0.1% HOAc for 5 h. When there was no ammonia in the reaction, protonated thiadiazine (m/z 193) was the dominant product (Figure 5a) similar to the above results (Figure 3). However, when 0.1% (v/v) ammonia was introduced into the reaction system (pH 8.45), a noticeable and intensive peak at m/z 185 emerged and overwhelmed the others (Figure 5b). Increasing the amount of ammonia in solution led initially to an increase in its intensity followed by a decreasing trend (Figure 5b-f). When the percentage of ammonia was 0.5% in the solution (pH 8.91), the species at m/z 185 showed the strongest signal (Figure 5c), while the product was barely observed for the system with ammonia above 20% (pH > 11.21, Figure 5h). These results indicated this species was more stable in the solution with pH ranging from 8.45 to 9.43. Further enhancement of the pH (10.27 - 11.21) resulted in its gradual disappearance, presumably owing to decomposition.<sup>32</sup> Along with the emergence and disappearance of the species at m/z 185, the peak at m/z 141 showed the same pattern, but no direct correlation was noticed between their abundances (**Figure 5b-g**). In addition, when the peak at m/z 185 overwhelmed others in the mass spectrum, sodiated triazine at m/z 242 would disappear (**Figure 5b-d**). When the intensity of protonated thiadiazine (m/z 193) overwhelmed others, sodiated triazine could be seen again, and an extra peak at 279 appeared (**Figure 5e-h**). These results illustrate that the occurrence of the species at m/z 185 might be closely related to the ones at m/z 141, 242 and 269.

To gain an insight into the correlation between those species, it is necessary to validate their origins and corresponding structures. As the species at m/z 185 was the central one and originated from the reaction system involved with triazine, Na<sub>2</sub>S, HOAc and ammonia in acetonitrile, we studied the possible systems for its generation (Figure S12), and found that when triazine was mixed with ammonia, it could produce the species at m/z 185 (Figure 6a), suggesting that it stemmed from triazine and ammonia rather than other possibilities. Further investigation using high resolution mass spectrometry indicated that it had a composition of  $C_8H_{17}ON_4^+$  (m/z 185.1398, Figure 6b). According to the documented structures<sup>33</sup> of  $C_8H_{17}ON_4^+$  and possibility in the current system, 1-(2-hydroxyethyl)-3,5,7-triaza-1-azoniatricyclo[3.3.1.1<sup>3,7</sup>] decane (abbreviated as HTAD, Figure 6c) was speculated as the potential candidate. To confirm the chemical structure of the product  $C_8H_{17}ON_4^+$  (m/z 185) generated from triazine and ammonia, MS/MS analysis was carried out and the fragmentation pattern was compared with that from 1-(2hydroxyethyl)-3,5,7-triaza-1-azoniatricyclo[3.3.1.1<sup>3,7</sup>]decane bromide (Y11, standard sample). As demonstrated in Figure **6d** and **e**, both cations  $C_8H_{17}ON_4^+$  (m/z 185) have identical fragmentation patterns, and all generated fragments have comparable relative intensity. This further validates that the



**Figure 6. (a)** Mass spectrum of the solution from the reaction between 46  $\mu$ mol mL<sup>-1</sup> triazine and 1.0% ammonia using acetonitrile as solvent; **(b)** Mass spectrum of m/z 185.1398 with a composition of C<sub>8</sub>H<sub>17</sub>ON<sub>4</sub> using a high resolution Orbitrap mass spectrometer; **(c)** Structure of 1-(2-hydroxyethyl)-3,5,7-triaza-1-azoniatricyclo[3.3.1.1<sup>3,7</sup>]decane; MS/MS spectrum of the peak at m/z 185 **(d)** from the reaction between triazine and ammonia in acetonitrile and **(e)** from the standard sample 1-(2-hydroxyethyl)-3,5,7-triaza-1-azoniatricyclo[3.3.1.1<sup>3,7</sup>]decane bromide (named as Y11) with a concentration of 1.0  $\mu$ g mL<sup>-1</sup>; **(f)** Mass spectrum of the solution from the reaction between 46  $\mu$ mol mL<sup>-1</sup> triazine and 0.5% <sup>15</sup>N-labelled ammonia (<sup>15</sup>NH<sub>3</sub>·H<sub>2</sub>O) from <sup>15</sup>NH<sub>4</sub>Cl and NaOH using acetonitrile as solvent; **(g)** MS/MS spectrum of the peak m/z 188; **(h)** Mass spectrum of the solution from the reaction between 2.3  $\mu$ mol mL<sup>-1</sup> triazine and 1.0% ammonia using <sup>13</sup>C-labelled acetonitrile (<sup>13</sup>CH<sub>3</sub><sup>13</sup>CN) as solvent.

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product (m/z 185) has a structure of HTAD.

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In an attempt to identify the sources of nitrogen atoms and carbon atoms involved in the reaction, isotopically-labelled standard samples, including <sup>15</sup>N-labelled ammonium chloride (<sup>15</sup>NH<sub>3</sub>Cl) and <sup>13</sup>C-labelled acetonitrile (<sup>13</sup>CH<sub>3</sub><sup>13</sup>CN), were used. After a reaction period of 5 h, the peak at m/z 188 became dominant rather than the peak at m/z 185 when ammonia was produced by <sup>15</sup>N-labelled ammonium chloride and sodium hydroxide (Figure 6f and g). This revealed that three nitrogen atoms in the structure of  $C_8H_{17}ON_4^+$  (m/z 185) were from ammonia, and one nitrogen atom originated from triazine because no other nitrogen sources were involved in the reaction system. As <sup>13</sup>C-labelled acetonitrile was used as solvent, the primary peak was still m/z 185 (Figure 5h), suggesting that the carbon atoms in produced  $C_8H_{17}ON_4^+$  were all from triazine and that acetonitrile did not participate in the reaction.

Based on the above, the formation of  $C_8H_{17}ON_4^+$  appears to 17 involve the rearrangement or decomposition of triazine fol-18 lowed by a reaction with ammonia. Due to the similar struc-19 ture between HTAD (m/z 185,  $C_8H_{17}ON_4^+$ ) and hexamethyl-20 enetetramine (m/z 141,  $C_6H_{13}N_4^+$ ) as generated from formal-21 dehyde and ammonia,<sup>34</sup> we speculate that both species might 22 experience a similar reaction mechanism, undergoing an ad-23 dition and dehydration reaction. In the process, formalde-24 hyde plays a crucial role in determining the reaction, and it 25 could be produced in the current reaction system. If this de-26 duction is correct, hexamethylenetetramine (m/z 141) should 27 be produced along with HTAD (m/z 185). After careful exami-28 nation on Figure 5b-g, it could be found that with the emer-29 gence and disappearance of the species at m/z 185, another 30 species at m/z 141 behaved the same pattern although no 31 correlation exists between their abundances. Further evi-32 dence from high resolution mass spectrometry, MS/MS spec-33 tra, and standard sample comparison (Figure S13) indicates 34 that the species at m/z 141 has a possible structure of hexa-35 methylenetetramine. This suggests that formaldehyde (mo-36 lecular weight: 30 Da) was indeed produced in the current 37 reaction system. To obtain direct evidence on its production, we compared the mass spectra for the sample from the reac-38 tion between 0.23 µmol mL<sup>-1</sup> triazine and 0.5% ammonia us-39 ing a full scanning mode (Figure S14a) and a neutral loss 40 scanning mode with a loss of 30 Da (Figure S14b). The species 41 at m/z 186, 116, 86 and 74, if they undergo a neutral loss of 42 30 Da, produce peaks at m/z 156, 86, 56 and 44, and all those 43 species were observed in the mass spectrum with a full scan-44 ning mode (Figure S14a). Because of the close proximity be-45 tween the species at m/z 186 and the HTAD (m/z 185) as well 46 as the low intensity of the species at m/z 156 (Figure S14a), 47 we only studied the compositions of the peaks at m/z 116, 86, 48 74, 56 and 44. The results from their corresponding high reso-49 lution mass spectra (Figures S2b and b' and S14c-e) and 50 MS/MS spectra (Figures S14f-g) indicated that the neutral 51 loss unit (30 Da) from the species at m/z 116 (C<sub>5</sub>H<sub>10</sub>NO<sub>2</sub>, Fig-52 ure S14e), 86 ( $C_4H_8NO$ , Figure S14c) and 74 ( $C_3H_8NO$ , Figure 53 **S2b** and **b'**) indeed had a structure of CH<sub>2</sub>O, matching the 54 composition of formaldehyde. This further suggests that for-55 maldehyde is produced from the present reaction systems, 56 and, more importantly, there are several routes to generate it. 57 Because formaldehyde and ammonia were available, the pro-58



**Scheme 2.** Proposed Reaction Mechanism for the Production of 1-(2-Hydroxyethyl)-3,5,7-triaza-1-azoniatricyclo[3.3.1.1<sup>3,7</sup>]decane (XV, m/z 185) and Hexamethylenetetramine (XI, m/z 141).

duction of HTAD (m/z 185,  $C_8H_{17}ON_4^+$ ) and hexamethylenetetramine (m/z 141,  $C_6H_{13}N_4^+$ ) would be feasible.

According to the above results, possible reaction mechanisms for the generation of 1-(2-hydroxyethyl)-3,5,7-triaza-1azoniatricyclo[3.3.1.1<sup>3,7</sup>] decane (HTAD, m/z 185) and hexamethylenetetramine (m/z 141) are proposed as Scheme 2. The generation of formaldehyde plays a vital role in this process. Because the abundances of the species at m/z 86 and m/z 74 are more dominant than those of others (Figure S14a), herein we only describe the pathways from them to the production of formaldehyde followed by reaction with 2hydroxy-N-methyleneethanaminium (m/z 74) and/or ammonia. For the pathway from the species at m/z 86 (namely Pathway A), sodium (I) would first attack triazine (I) with the generation of V (m/z 242), which turns into VI (m/z 218) by loss of NaH and isomerization. V would produce VIII (m/z 86) with a loss of VII through a structural rearrangement. Further neutral loss leads to the formation of IX (m/z 56) and formaldehyde (X). For the Pathway B, triazine (I) or protonated triazine (XII, m/z 220) would first undergo hydrolysis by generation of XIII (m/z 74). After rearrangement, XIII would lead to the formation of XIV (m/z 44) and formaldehyde (X). After the generation of formaldehyde, on the one hand, XIII (m/z) would react with it and ammonia by production of HTAD (m/z 185) under the pH range of 8.45 - 9.43. Further increasing the pH value up to 10.27 would result in the decomposition of HTAD, which is not favorable to its observation (Figure 5). On the other hand, formaldehyde would react with ammonia by formation of hexamethylenetetramine (XI, m/z 141) after a series of addition and dehydration reactions as reported by Butlerow.<sup>35</sup> Despite of the similar structure between HTAD and hexamethylenetetramine, further investigation through <sup>15</sup>N-labled experiments indicated that hexamethylenetetramine was produced by the reaction between ammonia and generated formaldehyde (Figure S15), and did not originate from HTAD by loss of hydroxyethyl group.

#### 3. CONCLUSIONS

In summary, we performed a systematic investigation on the reaction mechanism between triazine and  $H_2S$  with pH varia-

tion in solution using paper spray MS. We show that the reac-1 tion solvent plays a crucial role in determining the MS meas-2 urement, in which an aprotic solvent (e.g., acetonitrile, ace-3 tone, ethyl ether and ethyl acetate) is more advantageous to 4 the observation of reaction intermediates than a protic sol-5 vent (e.g., methanol, water, ethanol and propanol) owing to 6 hydrogen bond interaction. With variation in the pH value of 7 reaction solution, completely different pathways were ob-8 served. As the pH ranged from 5.58 to 7.73, triazine reacted 9 with H<sub>2</sub>S by generation of thiadiazine, where a nitrogen atom was substituted with a sulfur atom. With a decrease in the pH 10 to 3.02 - 3.69, the reaction pathways differed from the tradi-11 tional ones, and the major product was 2-(5-(2-hydroxyethyl)-12 1,3,5-thiadiazinan-3-yl)acetaldehyde converted from thiadia-13 zine. When ammonia was added into the reaction system and 14 the pH was adjusted to 8.45 - 9.43, the formed intermediate 15 from the hydrolysis of triazine would favorably react with 16 ammonia and formaldehyde in situ from triazine to generate 17 1-(2-hydroxyethyl)-3,5,7-triaza-1-azoniatricyclo  $[3.3.1.1^{3,7}]$ 18 decane (HTAD) along with the formation of hexamethylene-19 tetramine. Further increasing the pH up to 10.27 - 11.21 led 20 to their disappearances due to decomposition. According to 21 the experimental observation and evidence from high resolu-22 tion and tandem mass spectrometry, isotopically-labelled 23 experiments and standard sample comparison, plausible 24 mechanisms were proposed for the first time to elucidate the 25 reaction pathways between triazine and H<sub>2</sub>S and the derived 26 reaction from triazine with pH variation in solution. In con-27 trast to the previous reports, 1,3,6,7,10 the current study not only 28 gives a more comprehensive view on understanding the 29 pathways between triazine and H<sub>2</sub>S with change in the pH of 30 the reaction solution, but also provides an experimental basis 31 on how to control the pH value in order to prevent triazine 32 from hydrolysis and enhance the reaction efficiency between 33 it and H<sub>2</sub>S. 34

#### EXPERIMENTAL SECTION

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36 Materials. All the necessary chemicals were from commer-37 cially available sources. Triazine, sodium sulfide (Na<sub>2</sub>S·9H<sub>2</sub>O), 38 ammonia solution (28% in water), sodium hydroxide and ammonium chloride were purchased from Beijing InnoChem 39 Science & Technology Co. Ltd. (Beijing, China), Tianjin Fuchen 40 Chemical Reagents Factory (Tianjin, China), Zhengzhou Paini 41 Chemical Reagent Factory (Zhengzhou, China) and Tianjin 42 Kemiou Chemical Reagent Co., Ltd. (Tianjin, China), respec-43 tively. <sup>15</sup>N-labled ammonium chloride (<sup>15</sup>NH₄Cl, ≥98.5%), 1,2-44 <sup>13</sup>C<sub>2</sub>-acetonitrile (<sup>13</sup>CH<sub>3</sub><sup>13</sup>CN, 99%) and 1-(2-hydroxyethyl)-45 3,5,7-triaza-1-azoniatricyclo[3.3.1.13,7]decane bromide (Y11, 46 ≥98%) and hexamethylenetetramine were purchased from 47 Shanghai Research Institute of Chemical Industry (Shanghai, 48 China), Cambridge Isotope Laboratories, Inc. (Andover, MA, 49 USA), Sigma-Aldrich Inc. (Milwaukee, WI, USA) and Shaanxi 50 Pioneer Biotech Co,. Ltd. (Xi'an, China), respectively. The sol-51 vents, including methanol, acetonitrile, acetic acid, ethyl 52 ether, ethyl acetate, ethanol and propanol, were purchased 53 from Beijing J&K Scientific Ltd. (Beijing, China). Filter paper 54 was purchased from Hangzhou Special Paper Co. (Fuyang, 55 China). 56

**Preparation of Reaction Solution with Variation in Acidity.** Quantitative transfer of 5  $\mu$ L of 46  $\mu$ mol mL<sup>-1</sup> triazine aqueous solution into a series of acetonitrile solutions (990, 989, 985, 980, 940 and 890  $\mu$ L) was followed by adding 5  $\mu$ L of 46  $\mu$ mol mL<sup>-1</sup> Na<sub>2</sub>S aqueous solution. Then different volumes of acetic acid solution (0, 1, 5, 10, 50 and 100  $\mu$ L) were added into the above solution, giving volume percentage of acetic acid of 0%, 0.1%, 0.5%, 1%, 5% and 10% (v/v), respectively. After mixing for 1 min with a QL-901 vortex mixer (Haimen Kylin-Bell Lab Instruments Co., Ltd, Haimen, China), the above solution was maintained at room temperature for 5 h under static conditions, in preparation for later analysis.

Preparation of Reaction Solution with Variation in Basicity. Analogous to the above procedure for preparing the reaction solution with various acidities, we first prepared a reaction solution with 0.23  $\mu$ mol mL<sup>-1</sup> triazine and 0.23  $\mu$ mol mL<sup>-1</sup> Na<sub>2</sub>S followed by adding 1  $\mu$ L acetic acid into it. After mixing thoroughly and then maintaining at room temperature for 5 h, we quantitatively transferred different volumes of reaction solutions (999, 995, 990, 950, 900, 850 and 800  $\mu$ L) into 1.5 mL centrifugal tubes. Subsequently, adding various volumes of 28% ammonia solution (1, 5, 10, 50, 100, 150 and 200  $\mu$ L) into the above solutions, respectively, gave percentages of ammonia in solutions of 0.1%, 0.5%, 1%, 5%, 10%, 15% and 20% (v/v), respectively. After mixing for 1 min with a vortex mixer, the above solutions were maintained at room temperature for 30 min under static conditions followed by MS analysis.

**Preparation of the Reaction Solution of Triazine and Ammonia from Ammonium Chloride and Sodium Hydroxide.** We first dissolved 0.25 g ammonium chloride (<sup>14</sup>NH<sub>4</sub>Cl or <sup>15</sup>NH<sub>4</sub>Cl) into 1 mL deionized water followed by adding 0.2 g sodium hydroxide. After mixing thoroughly, 5  $\mu$ L of the prepared solution and 5  $\mu$ L of 0.23  $\mu$ mol mL<sup>-1</sup> triazine were transferred into 990  $\mu$ L acetonitrile. Afterwards, the above solution was mixed and maintained at room temperature for 5 h under static conditions followed by analysis.

MS Analysis. All experiments on paper spray MS were carried out either with a TSQ Quantum Access Max mass spectrometer or with an Orbitrap Elite<sup>™</sup> Hybrid Ion Trap-Orbitrap Mass Spectrometer (Thermo Fisher Scientific, San Jose, CA). For paper spray, filter paper was directly cut into a triangle (around 13 mm height and 9 mm base width). The distance between the tip of paper triangle and the MS inlet capillary was about 15 mm. Mass spectra were recorded in the positive ion mode with a capillary temperature of 270 °C. The identification of analyte ions was confirmed by tandem mass spectrometry (MS/MS) using collision-induced dissociation (CID). Argon gas (99.995% purity) was used as the collision gas.

#### ASSOCIATED CONTENT

#### **Supporting Information**

Supporting Information Available: mass spectra of the reaction solutions under various experimental conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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