Intercalation of Methylamines into Titanium Disulfide

Lori A. Brown

Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287-1604

William S. Glaunsinger[1]

Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287-1604

E-mail: WGlaunsinger@asu.edu

and

Michael J. McKelvy

Center for Solid State Science, Arizona State University, Tempe, Arizona 85287-1704

E-mail: Michael.McKelvy@asu.edu

The reactions of methylamine, dimethylamine, and trimethylamine with TiS_2 were characterized by several techniques. Detailed studies of the intercalation of methylamine demonstrated that the reaction was of the redox-rearrangement type, where the intercalate is best described as $(CH_3NH_3^+)_{y'}$ $(CH_3NH_2)_{y''} TiS_2^{y'-}$, with $y' = 0.25 \pm 0.02$ and y'' dependent on sample history. For $y' = 0.25$ and $y'' = 0.15$, this intercalate is a mixed-phase stage 1 [$a = 3.422(5)$ Å and $c = 28.06(10)$ Å] and stage 2 [$a = 3.4265$ Å and $c = 42.48(10)$ Å] compound having $R\bar{3}m$ symmetry. Visual observation and thermogravimetric analysis of dimethylamine intercalation also suggest a redox-rearrangement mechanism. In contrast, no intercalation was observed for trimethylamine. The onset time for intercalation of liquid amines into TiS_2 at ambient temperature follows the general trend: $N_2H_4 < NH_3 < CH_3NH_2 < (CH_3)_2NH \ll (CH_3)_3N$. This trend is consistent with an increase in steric hindrance about the N atom and decrease in the number of amine hydrogen atoms that effectively reduces the nucleophilic reaction rate of the intercalant. © 2000 Academic Press
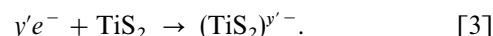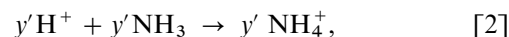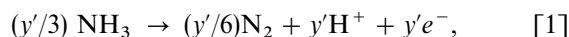
Key Words: intercalation reactions; methylamines; titanium disulfide.

INTRODUCTION

Intercalation compounds of the layered transition metal dichalcogenides (TX_2) have been of interest from both technological and fundamental scientific viewpoints.

Applications of these materials include high-energy-density batteries (1, 2), lubrication (3), catalysis (4), and photoelectrolysis (5). They also exhibit unusual properties, including anisotropic superconductivity and charge-density waves (6–8). Unlike the amphoteric host graphite, which can intercalate both electron acceptors and donors, only electron-donating species, such as electropositive metals and Lewis bases, have been intercalated into TX_2 hosts. One of the most extensively investigated reactions has been the prototypical Lewis base, ammonia, with transition metal disulfide (TS_2) hosts (9–23). However, even the behavior of this simple intercalant is complicated due to the wide variety of NH_3 molecular motions (11, 16, 17, 24), an unusual NH_3 geometry (24, 25), and redox reactions producing NH_4^+ (18, 22, 26).
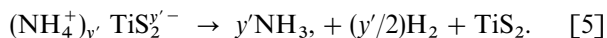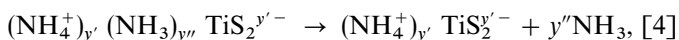
Redox reactions are widely applicable to molecular intercalation reactions with TS_2 hosts. In particular, such reactions have been shown to accompany NH_3 intercalation into TaS_2, TiS_2, and NbS_2 (18, 22, 26). The following redox-rearrangement reactions appear to accompany NH_3 intercalation of TiS_2:

$$(y'/3) NH_3 \rightarrow (y'/6)N_2 + y'H^+ + y'e^-, \qquad [1]$$

$$y'H^+ + y'NH_3 \rightarrow y' NH_4^+, \qquad [2]$$

$$y'e^- + TiS_2 \rightarrow (TiS_2)^{y'-}. \qquad [3]$$

The resulting intercalation compounds have the general formula $(NH_4^+)_{y'}(NH_3)_{y''}TiS_2^{y'-}$, where $y' = 0.22 \pm 0.02$ [22]. Thermal deintercalation of $(NH_4^+)_{y'} (NH_3)_{y''} TiS_2^{y'-}$

proceeds by a two-step mechanism, as shown below:

$$(NH_4^+)_{y'} (NH_3)_{y''} \, TiS_2^{y'-} \rightarrow (NH_4^+)_{y'} \, TiS_2^{y'-} + y''NH_3, \quad [4]$$

$$(NH_4^+)_{y'} \, TiS_2^{y'-} \rightarrow y'NH_3, + (y'/2)H_2 + TiS_2. \quad [5]$$

Lewis bases that are structurally and chemically similar to NH_3, such as the simple alkylamines, are also known to intercalate into TX_2 hosts (27). Substitution of relatively unreactive methyl groups for one or more of the protons in NH_3 is expected to modify substantially its intercalation chemistry. The primary focus for this work was to explore the intercalation chemistry of methylamine in the thoroughly characterized TiS_2 host, whose ammonia intercalation chemistry has already been extensively investigated (22). Preliminary investigations of the reactivity of dimethylamine and trimethylamine were also undertaken to provide a better understanding of amine intercalation chemistry.

EXPERIMENTAL

Methylamine (99.9%), dimethylamine (99%), and trimethylamine (99%) were purchased from Aldrich Chemical Company. All vacuum fittings employed were first sonicated three times in both toluene and acetone to remove any oils used in processing and to ensure a dry means of transfer of the material into the storage vessel. The reagents were condensed over Li metal to remove the last traces of water. A blue color resulting from the solvation of electrons in the CH_3NH_2 solution was an indication of dryness. Since Li is less soluble in $(CH_3)_2NH$ and $(CH_3)_3N$, these solutions required vigorous swirling to ensure that the last traces of water were removed from the reagent. The shiny surface of the metal was an indicator of dryness for these solvents. Prior to use, the reagent was cooled to liquid-nitrogen temperature several times, and each time the system was evacuated at 10^{-6} Torr to remove any residual H_2.

All samples were prepared, handled, and investigated under rigorous inert-atmosphere conditions due to their extreme air and water sensitivity (28). All reactions were carried out at ambient temperature via liquid-phase intercalation. Increasing the reaction temperature promoted sample degradation and, consequently, was abandoned. Intercalation of bulk samples was indicated by the following *in situ* observations: swelling of the sample, flocculation of particles, evolution of a gas, color change in the solution, and/or color change in the compound.

The stoichiometries of volatile components of the TiS_2 intercalation compounds were investigated by thermogravimetric analysis (TGA), vapor pressure measurements (VPM), and evolved gas analysis (EGA) (29). Samples were hermetically sealed in aluminum pans in the glovebox, weighed to the nearest 0.1 mg, and transferred to the TGA using glass weighing bottles placed into a tightly sealed inert-atmosphere container. The TGA was encased in a homemade glovebox and flushed with N_2 before the sample was transferred to the TGA balance. The sample pans were pierced immediately prior to analysis to permit escape of volatile species. The flow gas was ultrapure (99.999%) argon, which was further purified by passing it through a titanium-metal purifier at 925°C. Thermal analysis runs were started several minutes after the TGA gas-flow system was closed to allow the N_2 from the outer glovebox to be displaced by the flowing Ar in the TGA.

X-ray powder diffraction (XPD) patterns were collected to confirm intercalation and determine the lattice parameters. Samples were sealed in 0.3-mm Pyrex capillaries in a He-filled Vacuum Atmospheres, Inc., glovebox (≤ 1 ppm O_2 and H_2O), and the patterns were collected on a rotating-anode diffractometer using $MoK_{\alpha 1}$ ($\lambda = 0.7093$ Å) and $K_{\alpha 2}$ ($\lambda = 0.7135$ Å) radiation. NIST 660 LaB_6 was used for calibration. Refinement of the lattice parameters was performed by the Rietveld method using the generalized crystal structure analysis system (30–31).

Vapor pressure measurements were made on a vacuum line connected to a Baratron gauge. The entire system had an average static leak rate of less than 6 m Torr/h. Mass spectra of the evolved gases were obtained using a Hiden residual gas analyzer interfaced to the vacuum system.

RESULTS AND DISCUSSION

1. Methylamine intercalation. After several hours of contact with liquid CH_3NH_2, the TiS_2 sample height remained constant, the solution was colorless, and there was no change in the sample color that would indicate the onset of intercalation. In contrast, layer expansion of bulk TiS_2 is initiated within 20 min after contact with liquid NH_3 and is nearly complete after 2 h (32). Ammonium intercalation occurs at a slower rate and requires extended reaction times to reach the equilibrium NH_4^+ concentration of $y' = 0.25$ (32). The onset of CH_3NH_2 intercalation was indicated by expansion of the material after approximately 10 h. In addition, a pale blue-green solution color developed that signaled polysulfide formation. Such formation of polysulfides can accompany redox-rearrangement intercalation, as found for the silver–ammonia intercalates of TiS_2 (33). The latter compounds are prepared by reaction of $Ag_x TiS_2$ with liquid NH_3. The product is best described by the ionic formula $Ag_x^+(NH_4^+)_{y'}(NH_3)_{y''}TiS_2^{(x+y')-}$, where $x + y' = 0.24 \pm 0.02$. Hence, the extent of NH_4^+ formation is dependent on the Ag concentration. For $y' = 0$, i.e., $Ag_{0.25}(NH_3)_y TiS_2^{0.25-}$, polysulfide formation is not observed. Therefore, formation of polysulfides in NH_3 and CH_3NH_2 intercalation of TiS_2 is indicative of redox-rearrangement reactions.

EGA of noncondensable gases at liquid-nitrogen temperature for samples reacted for longer than 1 months revealed

less than 0.1 mol% N_2 per mole TiS_2, compared to 3.8 mol% N_2 for $(NH_4^+)_{0.23}(NH_3)_{y''}TiS_2^{0.23-}$ (28). Assuming that redox reactions analogous to Eqs. [1]–[3] are valid, this would correspond to $y' = 0.006$, which suggests essentially no redox-arrangement reaction for intercalation of CH_3NH_2 into TiS_2. However, the reaction does not appear to be purely molecular on the basis of visual observations.

The residual gas analysis (RGA) spectrum of volatile species in the pale blue-green solution compared favorably to reagent methylamine, as shown in Figs. 1a and 1c. After 2 days, the methylamine above TiS_2 turned a brownish-yellow color that deepened further with time. RGA of this liquid revealed the presence of trace species at 41, 42, and 43 amu, as shown in Fig. 1b. The identity of these species has not been resolved. However, these species were not observed for reaction periods less than 2 days.

The XPD pattern of nominally $(CH_3NH_2)_{0.40 \pm 0.05}TiS_2$, as determined by VPM, was refined as a $R\bar{3}m$ mixed-phase stage 1 [$a = 3.422(5)$ Å and $c = 28.060(10)$ Å] and stage 2 [$a = 3.426(5)$ Å and $c = 42.480(10)$ Å] compound. Substantial peak broadening is observed, consistent with layer disorder and staging phenomena that are both known for similar materials (34, 35). For example, $(NH_4^+)_{y'}(NH_3)_{y''}TiS_2^{y-}$ forms a single stage 1 phase for $y = y' + y'' > 0.56$

and a stage 2 phase for $y' \sim 0.25$ (32). Mixed phases are observed for $0.56 > y > 0.25$ (36). Therefore, observation of stage 1 and stage 2 phases for $(CH_3NH_2)_{0.40 \pm 0.05}TiS_2$ is similar to ammonia–TiS_2 intercalates. The presence of the stage 2 phase even after several hours of exposure of TiS_2 to an excess of CH_3NH_2 could be due to larger particles of TiS_2 in the sample, which cannot intercalate completely to form a stage 1 phase. In this case, more extended reaction times or high-pressure exposure of TiS_2 to CH_3NH_2 or using ultrafine particles of TiS_2 for the reaction could result in a pure stage 1 phase.

The a lattice parameter is an indication of guest–host charge transfer, as demonstrated by ammoniated TX_2 compounds (28, 37). The a lattice parameter for the methylamine–TiS_2 intercalate is in good agreement with a charge transfer of approximately 0.25 mol e^-/mol TiS_2. In addition, the difference in occupied layer expansion (ΔOLE) for stage 1 methylamine–TiS_2 (OLE = 3.66 Å) compared to ammonia–TiS_2 (OLE = 3.21 Å) is 0.45 Å. This is slightly larger than methylamine intercalates of $2H$–NbS_2 ($\Delta OLE = 0.34$ Å) (26, 38). The OLE for the stage 2 phase of $(CH_3NH_2)_{0.40 \pm 0.05}TiS_2$ (2.77 Å) is slightly larger than that for $(NH_4^+)_{0.21}TiS_2$ (2.54 Å), as anticipated from the larger size of the methyl group.

A representative TGA curve for monomethylamine samples reacted between 1 and 2 days with liquid CH_3NH_2 shown in Figure 2a is similar to the TGA curve for deintercalation of $(NH_4^+)_{0.22}(NH_3)_{0.23}TiS_2^{y-}$ in Fig. 2b. Guest species begin to desorb from the methylamine intercalate at relatively low temperatures ($< 50°C$), similar to NH_3 deintercalation, as shown in Fig. 2b.

Vapor pressure measurements of methylamine intercalate samples heated to 180°C show the gases evolved in the first step are entirely condensable at liquid-nitrogen temperatures. The mass spectrum of reagent CH_3NH_2 was compared to the spectrum of all gases evolved between 25–180°C, as shown in Figs. 1c and 3a, respectively. The primary species was identified as CH_3NH_2, and the fracture pattern is in good agreement with that of reagent methylamine in Fig. 1c. The second TGA step in Fig. 2b corresponds to the deintercalation of NH_4^+ from $(NH_4^+)_{0.23}TiS_2^{0.23-}$ above 150°C quantitatively in a 1:2 mole ratio of H_2 to NH_3, respectively (27). Results for VPM and RGA show 98% of the volume of deintercalated gases collected between 180 and 320°C from the methylamine–TiS_2 system evolved below 246°C. These gases were identified as H_2 and CH_3NH_2 in a 1:2 mole ratio, as indicated in Figs. 3b and 3c, respectively.

Residual CH_3NH_2 from the walls of the mass spectrometer was observed in the spectrum of noncondensable gases in Fig. 3b. The mass spectrum of the remaining species (2%) evolved between 246 and 320°C included peaks observed as 45 and 59 amu that originate from $(CH_3)_2NH$ and $(CH_3)_3N$, respectively, as seen in Fig. 3d. In addition to methylamine,
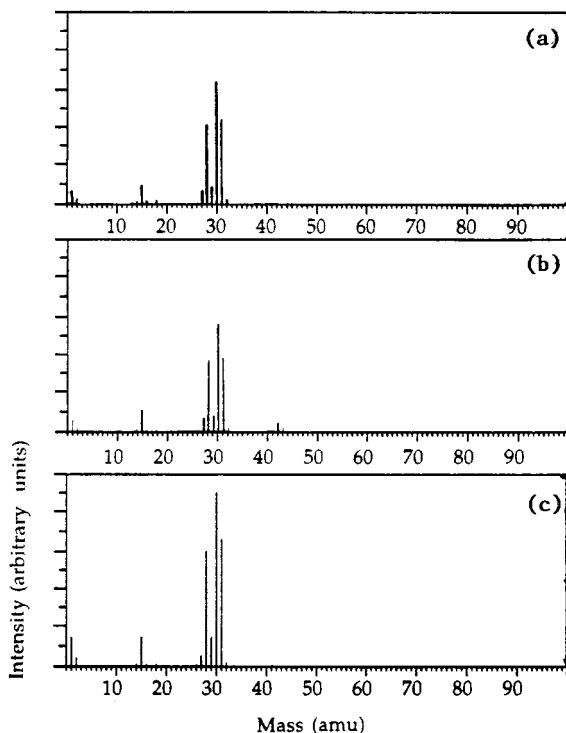

FIG. 1. Mass spectrum of (a) pale blue-green solution formed during reaction of methylamine with TiS_2 compared to (b) the brownish-yellow solution formed for reaction times exceeding 1 month of methylamine with TiS_2 and (c) reagent methylamine.
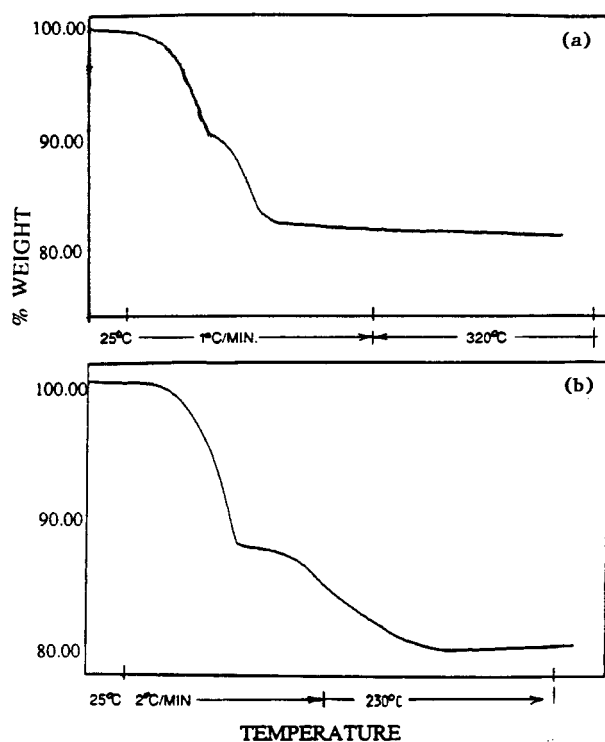
FIG. 2. Thermogram of the deintercalation of (a) nominally $(CH_3NH_2)_{0.52}TiS_2$ and (b) $(NH_4^+)_{0.22}(NH_3)_{0.23}TiS_2^{0.22-}$. The first step of both curves is associated with the removal of molecular guest species at low temperatures, where the concentration is dependent upon sample history. The second step of both curves represents the deintercalation of ionic species as 1:2 H_2 and CH_3NH_2 or NH_3, respectively.

stoichiometric $Ti_{1.002 \pm 0.001}S_2$. This corresponds to approximately 1 mol% $CH_3NH_3^+$ remaining in the host. Hence, the intercalation process is nearly reversible and, therefore, the intercalation product is best described

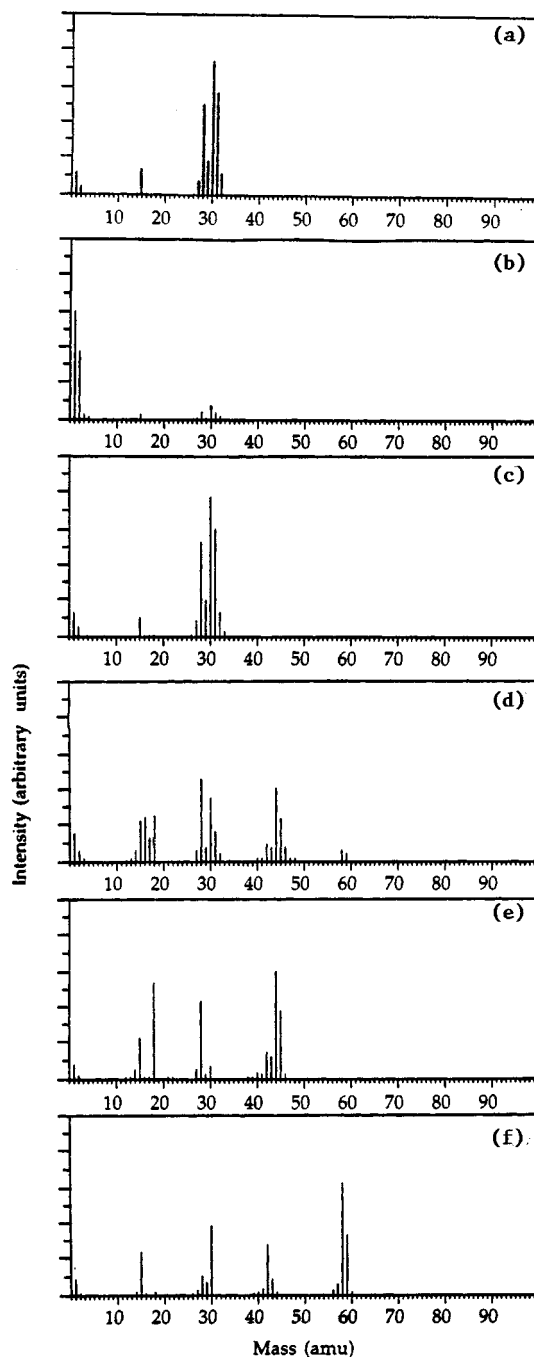the mass spectra of dimethylamine and trimethylamine standards were observed, as shown in Figs. 3e and 3f, respectively. Both species contribute to the mass spectrum in Fig. 3d. The presence of these higher-weight molecular species may provide a source for protonation of methylamine to form methylammonium during redox rearrangement, with minimal N_2 formation. The peaks at 16 and 17 amu in Fig. 3d were tentatively assigned to NH_3, which may result from breaking the C–N bond in CH_3NH_2. The fracture pattern for CH_3 cannot be distinguished from that of CH_3NH_2. The presence of NH_3 is not considered a primary source of protons for methylammonium formed during intercalation because NH_3 was not present in significant concentrations, as shown, for example, in Fig. 1c. The peak at 18 amu in Fig. 3d is associated with the fracture pattern of dimethylamine, as shown in Fig. 3e. The secondary peak at 32 amu observed in Figs. 3a, 3c, and 3d is tentatively assigned to N_2H_4.

Above 340°C, the host begins to decompose, as indicated by the evolution of H_2S (27). The guest species were not completely desorbed at this temperature, as indicated by the slope of the TGA curve when expanded to a larger scale. Oxidation of the deintercalated host of TiO_2 gave a final weight of 71.22%, compared to 71.44% for nearly

FIG. 3. Mass spectra from deintercalation of nominally $(CH_3NH_2)_{0.52}TiS_2$: (a) all gases evolved below 180°C from deintercalation of nominally $(CH_3NH_2)_{0.52}TiS_2$, (b) noncondensable gases evolved between 180 and 246°C, (c) condensable gases evolved between 180 and 246°C, (d) all gases evolved between 246 and 320°C, (e) reagent $(CH_3)_2NH$, and (f) reagent $(CH_3)_3N$.

using the ionic formula $(CH_3NH_3^+)_{0.25 \pm 0.02} (CH_3NH_2)_{y''}$ $TiS_2^{0.25 \pm 0.02-}$, where $0 < y'' < 0.35$. It is also noteworthy that the degree of charge transfer in these compounds is in close agreement with that found in $(NH_4^+)_{y'}(NH_3)_{y''}TiS_2^{y'-}$ (22), which indicates that intercalant size, geometry, and orientation differences do not influence the degree of charge transfer, as expected for redox-rearrangement intercalation.

2. Dimethylamine and trimethylamine intercalation. Intercalation of dimethylamine required several days before an expansion in the material was observed. There was no indication of gas evolution. However, a brownish-yellow solution similar to that observed for methylamine was formed. The intercalated host also appeared darker in color suggesting charge transfer to the host. The TGA deintercalation curve of the dimethylamine intercalate had three weight loss steps that suggest redox arrangement may occur for the dimethylamine–TiS_2 system. In contrast, trimethylamine gave no indication of reaction with TiS_2 after several months of contact with the liquid at ambient temperature. TGA "deintercalation" analysis of the isolated material gave $< 0.1\%$ weight loss, and oxidation of the heated sample gave the identical composition of the pristine host. However, preparation of $[(CH_3)_3N]_{0.3}NbS_2$ has been achieved by electrochemical intercalation (27).

There are three factors that may affect the reactivity of trimethylamine. First, and likely most importantly, there are no amine protons in $(CH_3)_3N$ to participate in redox rearrangement. Second, $(CH_3)_3N$ does not form hydrogen bonds, which have been shown to play a significant role in stabilizing transition metal dichalcogenide intercalation compounds (TMDICs) (25, 39). A third factor that may influence reactivity is the size of the guest due to the energy required to separate the layers. The OLE for ammonia and methylamine intercalation compounds of NbS_2 demonstrates this to be a rather small contribution. The OLE (3.02 Å) for $(NH_4)_{0.23}(NH_3)_{0.31}NbS_2^{0.23-}$ is in good agreement with the van der Waals (vdW) radius for NH_3 (26). NbS_2 layers are separated by an additional 0.32 Å in the methylamine intercalate, where the OLE for nominally $(CH_3NH_2)_{0.5}NbS_2$ is 3.34 Å (27). This increase is due to the size of the methyl group (vdW radius = 2.0 Å). Furthermore, the OLE (3.69 Å) for nominally $[(CH_3)_2NH]_{0.3}NbS_2$ is, in fact, greater than the OLE (3.62 Å) for $[(CH_3)_3N]_{0.3}NbS_2$ (27). This suggests that the decreased reactivity of trimethylamine, compared to dimethylamine, is not exclusively due to steric hindrance. It is noteworthy that hydrazine intercalation in TMDs is spontaneous, even though it is somewhat larger than NH_3 and cannot readily occupy individual guest sites (38). Wang *et al.*, suggest that the enhanced reactivity of hydrazine (40) may be due in part to strong preintercalation charge transfer (41). These observations underscore the significance of charge transfer during the early events of intercalation in TMDs.

CONCLUSION

The reactions of liquid alkylamines with TiS_2 were characterized by visual observation, EGA, XPD, TGA, and VPM. Samples reacted for extended times were observed to have a higher-molecular-weight species in the supernatant solution and exhibited multistep TGA curves that show the nature of guest species in this material to be dependent upon the reaction time and temperature. The focus of this study was, therefore, narrowed to limited reaction times at ambient temperature. None of the reactions exhibited reversible insertion of a single guest species. Polysulfide formation was observed for mono- and dimethylamine intercalation, which suggests these reactions are of the redox rearrangement type. The absence of reaction for trimethylamine suggests amine protons are essential for redox-rearrangement intercalation. The onset time for intercalation of liquid amines into TiS_2 at ambient temperature follows the following general trend: $N_2H_2 < NH_3 < CH_3NH_2 < (CH_3)_2NH \ll (CH_3)_3N$. This trend is consistent with an increase in steric hindrance about the N atom and a decrease in the number of amine hydrogen atoms. In particular, it is anticipated that the activation energy for intercalation should be rather low for good nucleophiles like NH_3, which can then attack the interlayer S–S van der Waals-type bonds to initiate intercalation via a bimolecular nucleophilic substitution reaction mechanism. Methylamines should also be good nucleophiles due to the electron-donating ability of methyl groups. However, intercalation reactivity is expected to decrease as a function of methyl substitution due to steric hindrance of methyl groups as well as a decrease in number of amine hydrogen atoms, as observed experimentally.

The intercalation of CH_3NH_2 into TiS_2 was studied in detail and was determined to be a redox-rearrangement reaction, with the intercalate best described as $(CH_3NH_3^+)_{y'}(CH_3NH_2)_{y''}TiS_2^{y'-}$, where $y' = 0.25 \pm 0.02$ and y'' is dependent on sample history. This value is comparable to the charge transfer observed in well-characterized ammoniated TiS_2. XPD data refinement shows the intercalate to be a $R\bar{3}m$ mixed-phase stage 1 [$a = 3.422(5)$ Å and $c = 28.06(10$ Å] and stage 2 [$a = 3.426(5)$ Å and $c = 42.48(10)$ Å] compound for $y' = 0.25$ and $y'' = 0.15$, respectively. The a lattice parameter determined from XPD data is consistent with approximately 25 mol% charge transfer. However, the reaction was not completely reversible using thermal methods. TGA results and visual observation of dimethylamine intercalation into TiS_2 suggest that this guest also undergoes a redox-rearrangement reaction.

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