



NMR Spectral Studies of Interactions Between the Accelerants SPS and MPS and Copper Chlorides

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Proton and C-13 NMR spectroscopic studies of possible interactions of the copper electroplating accelerant disodium bis(3-sulfopropyl)disulfide (SPS) and its reduced form sodium 3-mercaptopropylsulfonate (MPS) with both cuprous chloride and cupric chloride were carried out in 0.25 M D₂SO₄/D₂O with reagent concentrations between millimolar and 0.1 M under anaerobic conditions. It was confirmed that MPS reacted with CuCl to yield Cu(I)-thiolate products. No evidence for formation of a solution Cu(I)-SPS complex from CuCl and SPS was found. Instead, a redox reaction yielded a Cu(I)-thiolate along with Cu(II) with an estimated equilibrium constant of $5.2 \times 10^{-3} \text{ M}^{-1}$. The previously reported reaction of aqueous cupric chloride with MPS was investigated further under anaerobic conditions. In addition to SPS, Cu(I)-thiolate products similar to those from the CuCl/MPS reaction were identified. The reaction was found to be complete only upon addition of over 2 equiv of MPS. No evidence for any interaction between CuCl₂ and SPS was observed.

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Copper damascene through electroplating has become an important process in the electronics industry.¹ The importance of additives has long been recognized, and their mode of action continues to be of fundamental and practical interest. Although a large variety of useful levelers and inhibitors have been identified, relatively few effective accelerants are known. The most popular of these include disodium bis(3-sulfopropyl)disulfide (SPS) and its reduced form, sodium 3-mercaptopropylsulfonate (MPS). In the presence of chloride, these have been postulated to lift adsorbed inhibitors like polyethylene glycol from electrode surfaces and facilitate copper electrodeposition, possibly through the formation of a copper chloride-thiolate complex.¹

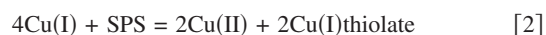
Healy and Pletcher² reported electrochemical studies indicating that SPS decomposed at open circuit to form a Cu(I)-thiolate complex in the absence of air. They also found that Cu(II) and MPS formed a green solution likely containing a similar Cu(I)-thiolate product. Subsequently, Survila et al.³ investigated the polarographic behavior of aqueous Cu(II) in the presence of MPS and calculated an equilibrium constant of $10^{3.3} \text{ M}$ for the reaction



In 2003, Frank and Bard⁴ electrolyzed a solution of Cu(II) with SPS and also reported the formation of a green solution whose electro-spray mass spectral data suggested the presence of an "SPS-Cu(I)" complex with retention of the SPS disulfide bond. By using UV-visible (UV-vis) and electron paramagnetic resonance spectroscopic data, they also found that Cu(II) with 2 equiv of MPS yielded a yellow solution but proposed a Cu(I)-MPS₂ product, although it was necessary to speculate that an additional oxidant was present to account for the formation of SPS. Schultz and co-workers⁵ used vibrational spectroscopic and mass spectral data augmented by density functional theory calculations to investigate the interactions of SPS/MPS with a copper surface both in the presence and absence of chloride. They proposed formation of a CuCl-SPS complex but with sulfonate rather than thiolate coordination and that the latter type of species is not an active component for observed acceleration behavior. Pasquale and co-workers⁶ reported in 2007 on the reaction of Cu(II) with 2 equiv of MPS to yield a yellow solution and characterized the postulated Cu(I)-thiolate product by UV-vis spectroscopy. However, aerobic workup of this reaction resulted in the isolation and full characterization of the fully oxidized Cu(II)-SO₃(CH₂)₃SO₃ complex. Okubu et al.⁷ used rotating ring-disk electrode (RRDE) data to suggest formation of two distinct Cu(I)-thiolates, one from SPS in the presence of chloride and the

other from MPS. In 2008, Chen and co-workers⁸ proposed the formation of a CuCl-MPS complex based on the electrochemical impedance spectroscopic data.

Despite these studies, much remains unclear about the nature of products from interactions between Cu(I)/Cu(II) and SPS/MPS accelerants and the extent of these reactions. Among the often postulated Reaction 1 and the following are of prime interest



As a first step toward gaining fresh insight into these fundamental solution accelerant-copper chloride interactions, we carried out proton and C-13 NMR spectroscopic studies of both cuprous and cupric chlorides with SPS and MPS under anaerobic conditions in 0.25 M D₂SO₄ solution. These were augmented by UV-visible spectroscopy to monitor Cu(II) concentrations. Potentiometric titrations were also carried out in aqueous solutions to gauge the amount of protons released in Reactions 1 and 3. Planned follow-up research will investigate the effect of oxygenation on these reactions and their products.

Experimental

All ¹H and ¹³C(¹H)-NMR spectra were acquired on either a Varian Mercury 400 MHz spectrometer operating at 399.75 and 100.51 MHz, respectively, or on a Varian Unity/INOVA 500 MHz spectrometer operating at 500 and 125.67 MHz, respectively. Chemical shifts were referenced to internal acetonitrile {¹H at δ 2.06

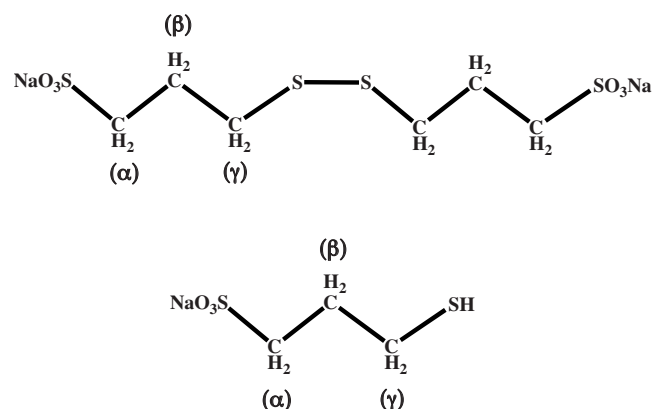


Figure 1. SPS and MPS.

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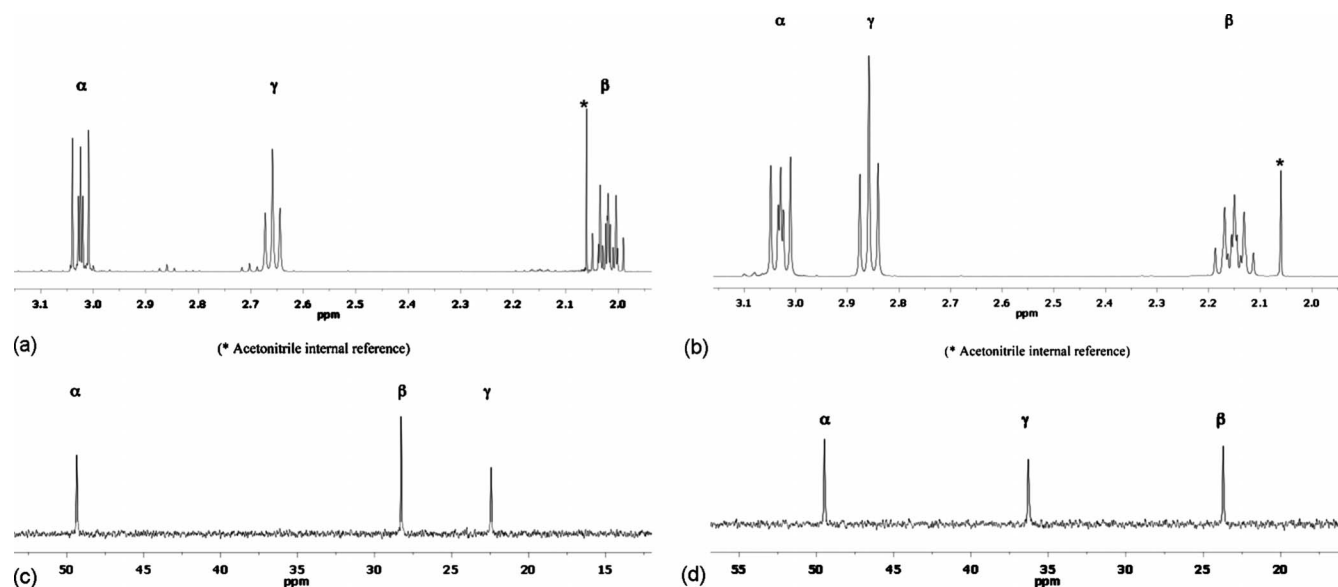


Figure 2. (a) Proton NMR spectrum of MPS in 0.25 M D_2SO_4 . (b) Proton NMR spectrum of SPS in 0.25 M D_2SO_4 . (c) $^{13}C\{^1H\}$ NMR spectrum of MPS in 0.25 M D_2SO_4 . (d) $^{13}C\{^1H\}$ NMR spectrum of SPS in 0.25 M D_2SO_4 .

and ^{13}C at δ 1.47}. A Cary 50 spectrophotometer was used for UV-visible spectral acquisition. D_2 -sulfuric acid and deuterium oxide were obtained from Sigma-Aldrich and Cambridge Isotope Laboratories, Inc., respectively. Potentiometric titrations were carried out in aqueous solution with a Metrohm Titrino 974 titrator under an argon atmosphere using standardized 0.1 M NaOH. All reactions and sample preparations were performed inside a vacuum atmosphere glove box under a prepurified nitrogen atmosphere.

Results and Discussion

In 0.25 M D_2SO_4 , both 0.1 M MPS and SPS gave well-resolved NMR spectra indicative of their three respective types of proton (α -, β -, and γ - CH_2 's relative to the sulfonate group: MPS δ 3.02/2.02/2.66; SPS δ 3.03/2.15/2.86) and C-13 (α -, β -, and γ - CH_2 's: MPS δ 49.35/28.27/22.42; SPS δ 49.49/23.71/36.31) environments (Figs. 1 and 2a-2d). We have acquired two-dimensional 1H - ^{13}C $gHMQC$ (gradient Heteronuclear Multiple Quantum Coherence) spectra to correlate and confirm respective proton and C-13 signal assignments. Note that these data for MPS correlated the furthest upfield C-13 resonance (δ 22.42) to the γ - CH_2 proton multiplet at δ 2.66 instead of the highest field β - CH_2 proton multiplet at δ 2.02 (Fig. 3). We thereby assigned this to be the γ -C resonance of

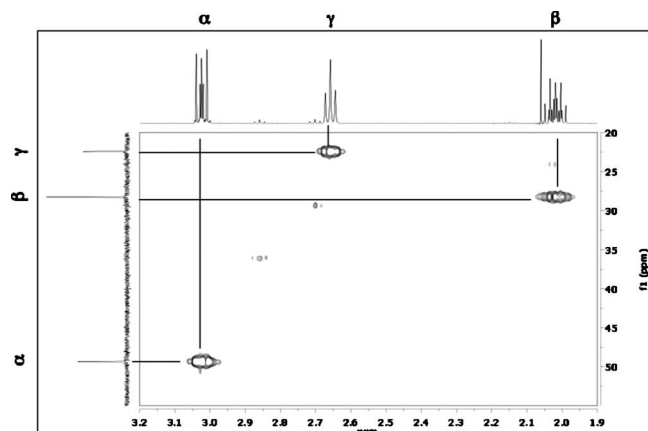


Figure 3. 1H - ^{13}C $gHMQC$ spectrum of MPS in 0.25 M D_2SO_4 .

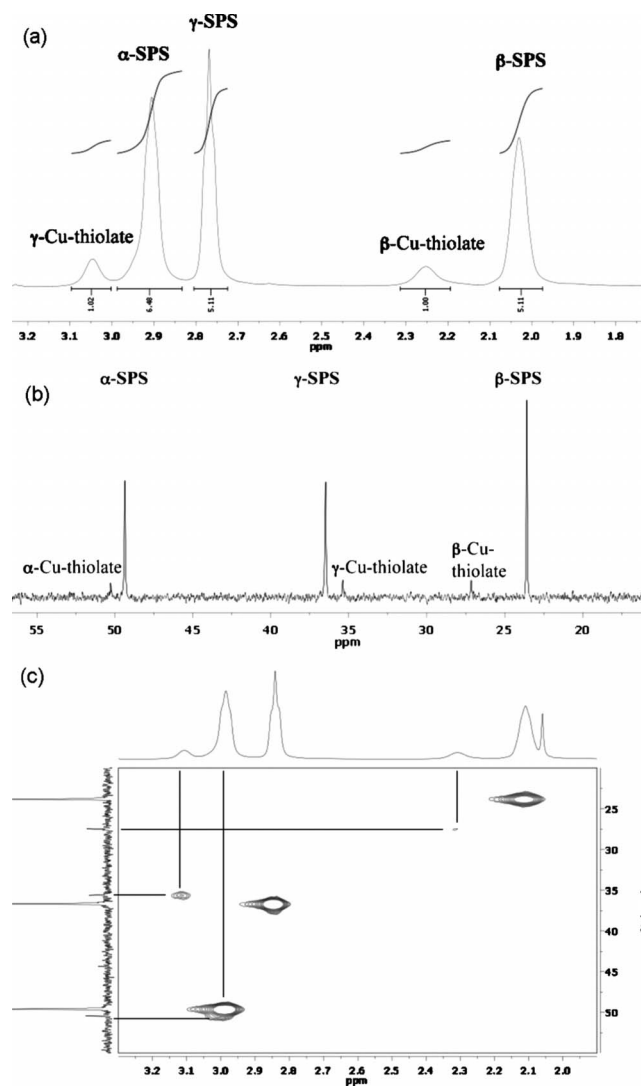


Figure 4. (a) Proton NMR spectrum of CuCl + SPS in 0.25 M D_2SO_4 . (b) $^{13}C\{^1H\}$ NMR spectrum of CuCl + SPS in 0.25 M D_2SO_4 . (c) 1H - ^{13}C $gHMQC$ spectrum of CuCl + SPS in 0.25 M D_2SO_4 .

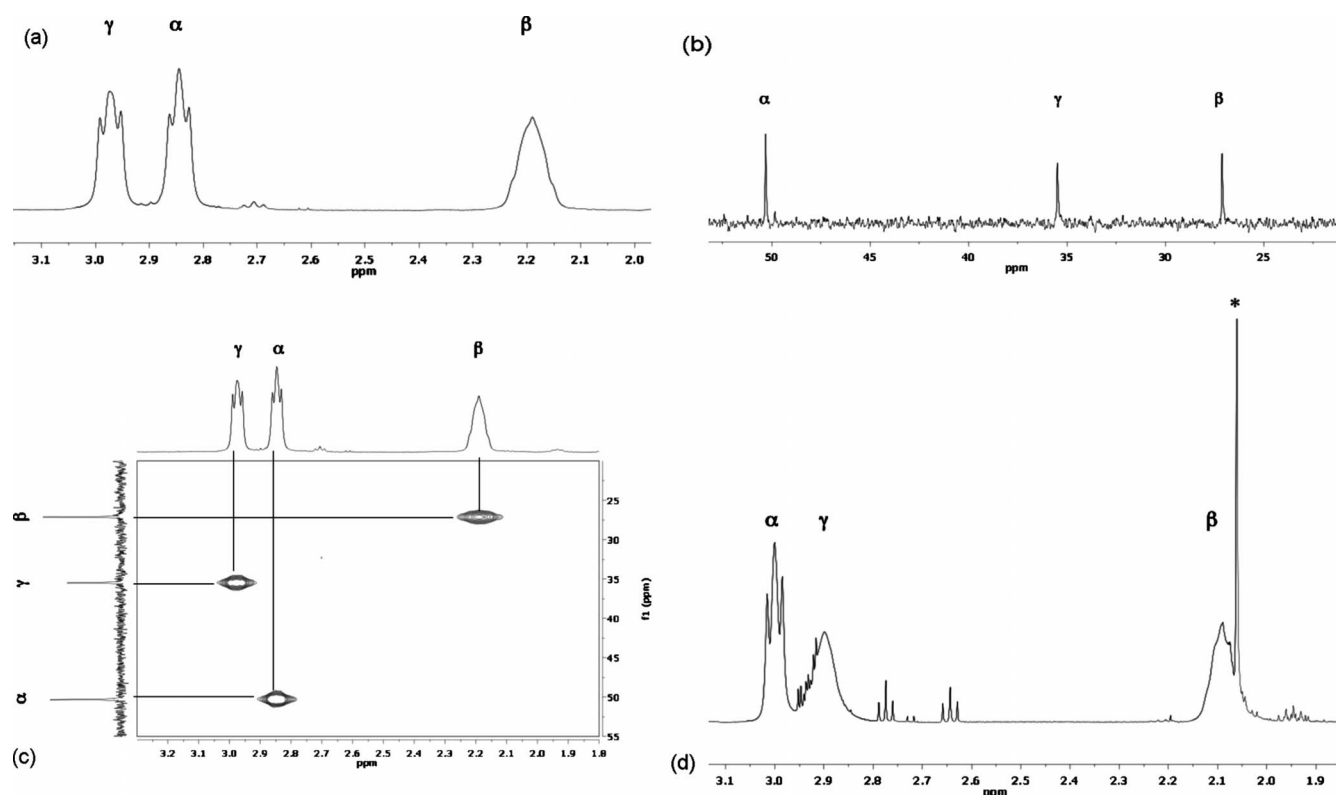


Figure 5. (a) Proton NMR spectrum of 2CuCl + MPS in 0.25 M D₂SO₄. (b) ¹³C{¹H} NMR spectrum of 2CuCl + MPS in 0.25 M D₂SO₄. (c) ¹H-¹³C gHMQC spectrum of 2CuCl + MPS in 0.25 M D₂SO₄. (d) Proton NMR spectrum of CuCl + MPS in 0.25 M D₂SO₄.

the methylene bonded to the thiol group.

Cuprous chloride and SPS (Reaction 2).—Reaction of an SPS solution (100 mM) in 0.25 M D₂SO₄ with an equivalent of CuCl beads required overnight stirring at room temperature to give a clear, light brown solution. The resulting proton NMR spectrum (Fig. 4) features three broadened SPS signals and a minor species (relative peak areas of ~5:1) with two broad resonances [δ 3.07 (γ - CH₂ shifted by +0.41 ppm relative to MPS) and 2.28 (β -CH₂ shifted by +0.26 ppm relative to MPS) plus a third inferred from the extra area of integration under the furthest downfield SPS resonance ($\sim\delta$ 2.95; Fig. 4a). The corresponding C-13 spectrum also shows a major and a minor component, the former consistent with free SPS while the minor species has three resonances at δ 50.28 (α)/35.40(γ)/27.15(β) (Fig. 4b).

Acquisition of a two-dimensional ¹H-¹³C gHMQC spectrum confirmed assignments of both major and minor resonances (Fig. 4c). There is a very sizable downfield shift of nearly 13 ppm for the γ -C (relative to MPS), which is consistent with the coordination by Cu(I) at the thiol while only small shifts are found for both α - and β -C resonances.⁹⁻¹² The minor species can, therefore, be assigned to be a Cu(I)-thiolate product.

Dilution of this NMR sample from 100 to 5 mM resulted in enhanced resolution of first the major and eventually the minor proton multiplets (spectrum not shown). These data are consistent with broadening of both unreacted SPS and the product Cu(I)-thiolate signals due to generation of paramagnetic Cu(II) in the redox process in Reaction 2. The presence of Cu(II) was further confirmed with UV-vis spectroscopy by an absorption maximum at 815 nm. Quantification using the measured absorbance and proton NMR spectral integration both yielded $K_2 = 5.2 \times 10^{-3} \text{ M}^{-1}$.

We found no evidence for the formation of any Cu(I)-SPS complex with retention of the disulfide bond. Experiments repeated in 0.5 M DCl gave essentially similar NMR spectra also inconsistent

with existence of a discrete CuCl-SPS complex in the solution. One would expect that in aqueous solution, Cu(I) should have little if any affinity for the very weakly basic and hard sulfonate anion. Instead, it would strongly prefer to coordinate at the much softer thiolate site.¹³ Although a sulfonate-coordinated CuCl-SPS complex cannot be ruled out in the solid state, only a single x-ray structure has been reported in the literature featuring Cu(I)'s coordinated to both chlorides and sulfonates.¹⁴ This rather unusual structure contains eight Cu(I)'s bridged by two tetraphosphines, six chlorides, and two terminal trifluoromethane sulfonates.

Cuprous chloride and MPS (Reaction 3).—Stirring a 0.25 M D₂SO₄ solution of MPS with 2 equiv of CuCl beads resulted in the rapid formation of a light canary yellow solution containing a product with similar proton and C-13 NMR spectra to the Cu-thiolate found in the CuCl/SPS reaction (Figs. 5a-5c). By contrast, reaction of MPS with 1 equiv of CuCl (90 mM in 0.25 M D₂SO₄) gave a proton NMR spectrum showing a slight broadening of the α -proton multiplet and significant broadening of both the β - and γ -methylene signals [δ 3.00 (bd t)/2.90 (bd s)/2.09 (bd s)] (Fig. 5d). A coordination shift of only +0.24 ppm was observed for the γ -resonance. Increasing the dilution of a similar NMR sample from 150 to 10 mM did not lead to the increased resolution of these β - and γ -signals, confirming that the observed broadening is not the result of nonspecific paramagnetic effects but rather due to an intermediate exchange rate on the NMR time scale between MPS and Cu(I)-thiolate species. Consistent with this, warming of a 90 mM CuCl:MPS sample to 90°C resulted in sharpening of both upfield resonances to yield fully resolved multiplets both shifted downfield from the parent MPS values ($\Delta\delta = +0.29$ and +0.12 ppm, respectively) (Fig. 6a).

Although no slow-exchange spectrum was obtainable, cooling a 90 mM sample to 0°C resulted in increased broadening of all proton signals and appearance of additional broad resonances again indica-

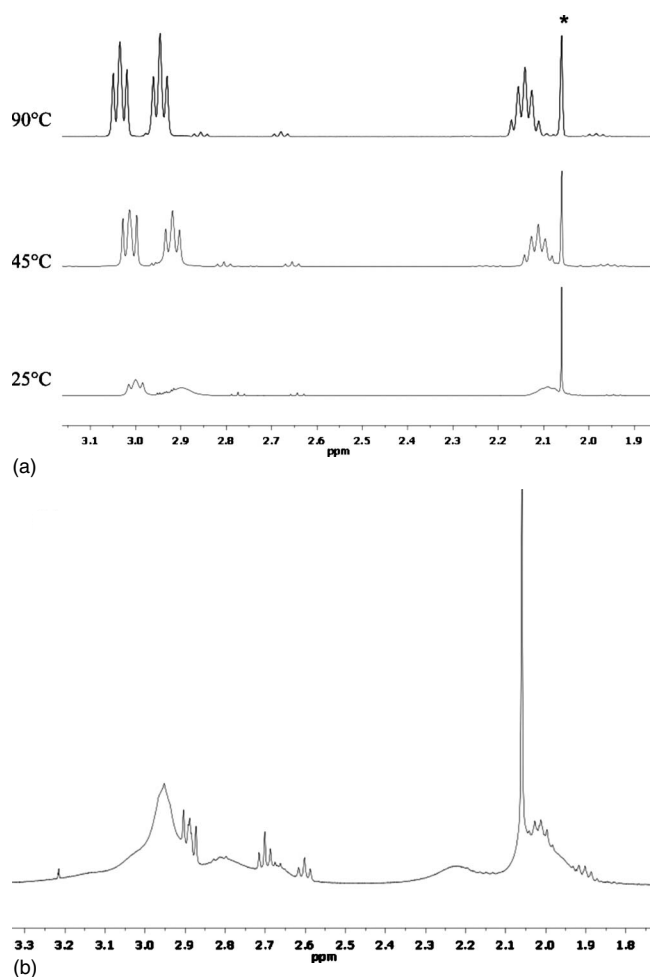


Figure 6. (a) High temperature proton NMR spectrum of CuCl + MPS in 0.25 M D_2SO_4 . (b) Low temperature proton NMR spectrum of CuCl + MPS in 0.25 M D_2SO_4 .

tive of intermediate exchange rates between multiple species containing the MPS moiety on the NMR time scale (Fig. 6b).

More sizable coordination shifts are noted in the averaged C-13 NMR spectrum of the 1:1 CuCl/MPS reaction [$\delta 50.30/\sim 32.5$ (γ)/29.03(β)], the γ -methylene resonance shifted downfield by more than 9 ppm and was significantly broadened as well. Interestingly, the β -C signal is also slightly broadened and underwent a coordination shift of +5.3 ppm (Fig. 7a). These assignments were confirmed by a two-dimensional 1H - ^{13}C *gHMQC* experiment (Fig. 7b). At 0°C, all three resonances are severely broadened, with the γ -signal in the baseline (spectrum not shown), again consistent with the slowing down of exchange between MPS-containing species.

Addition of extra equivalents of MPS to a 1:1 sample up to a ratio of 10:1 MPS:CuCl yielded averaged proton spectra with increasingly resolved γ - and β -CH₂ proton patterns approaching the free MPS spectrum shifts (Fig. 8a). Corresponding C-13 NMR spectral behavior was observed except that the γ -C signal remained severely broadened while moving upfield from δ 32 to nearly δ 24 (Fig. 8b; see also *gHMQC* Fig. 8c). These observations are also consistent with product Cu(I)-thiolate species in exchange with excess MPS.

Finally, CuCl and MPS aqueous solutions were titrated to assay the extent of Reaction 3 from the amount of protons released. It was found that a 1:1 stoichiometric reaction was only 80% complete with 0.8 equiv of protons produced. A 1:2 stoichiometry titration showed two end points; the first at *pH* 5.6 released exactly 1 proton

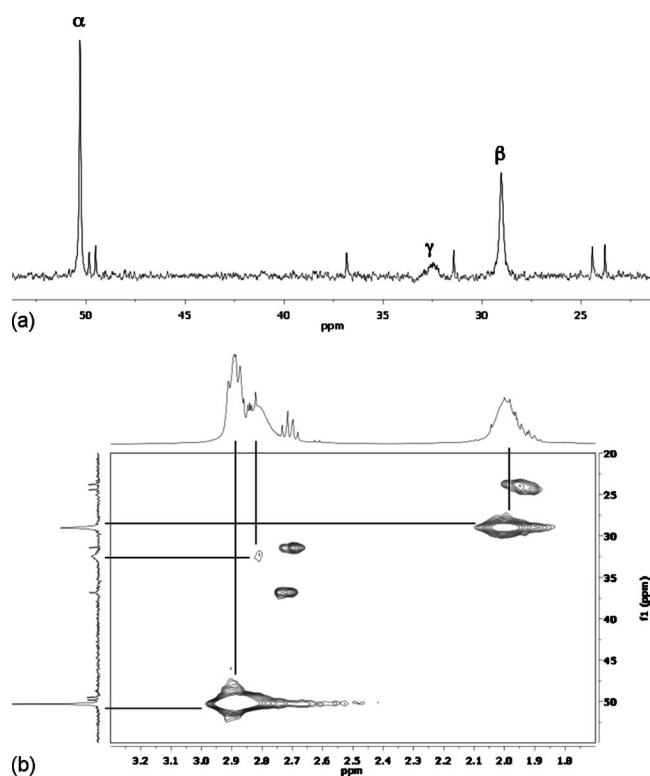


Figure 7. (a) $^{13}C\{^1H\}$ NMR spectrum of CuCl + MPS in 0.25 M D_2SO_4 . (b) 1H - ^{13}C *gHMQC* spectrum of CuCl + MPS in 0.25 M D_2SO_4 .

equiv while the second at *pH* 8.4 produced a further 0.2 equiv of protons. A 1:3 stoichiometry again yielded a first end point corresponding to 1 proton equiv with a second at *pH* 9.3 indicating release of an additional 0.4 proton equiv. These data indicate that formation of Cu(I)-(MPS)_{*n*} (*n* > 1) species can occur in the presence of excess MPS. Higher order cuprous thiolate products with varying stoichiometries have often been reported for reactions between Cu(I) and mercaptoethylsulfonate, cysteine, and other thiols.^{9-12,15-22}

Cupric chloride and MPS (Reaction 1).—Pasquale et al.⁶ previously reported the reaction of aqueous CuCl₂ with 2 equiv of MPS to give a yellow solution postulated to contain a Cu(I)-thiolate product according to Reaction 4. Aerobic workup of this, however, yielded the fully oxidized blue Cu(II)-SO₃(CH₂)₃SO₃ complex as a polymeric solid. Prior to this, Survila and co-workers³ used polarographic data to estimate a *K*₂ of 10^{3.3} for this equilibrium. To further investigate this chemistry, we have studied this reaction by NMR and electronic spectroscopy under anaerobic conditions. First, a spectrophotometric titration involving addition of MPS to CuCl₂ (68 mM in 0.25 M D_2SO_4) was carried out. Consistent with Pasquale's report, we note that although Cu(II) concentration decreased with increasing MPS, it was not consumed until more than 2 equiv of MPS were added (Fig. 9).

Proton NMR spectra of these reaction mixtures confirmed SPS formation and the presence of exchanging Cu(I)-thiolate/MPS species identical to those from the direct CuCl/MPS reaction described above (Fig. 10). Based on peak integrations, the Cu(I)-thiolate/MPS to SPS mole ratios are 1:2, 1:1.6, 1:1.2, and 1:0.67 upon the additions of 0.5, 1, 1.5, and 2 equiv of MPS, respectively.

An assay of released protons from these reactions in aqueous solution was then used to monitor Reaction 1 progress. A 1:2 stoichiometric reaction of 15 mM CuCl₂ with 30 mM MPS yielded the following data: UV-vis spectral assay of the Cu(II) concentration indicated about 90% consumption while potentiometric titration of

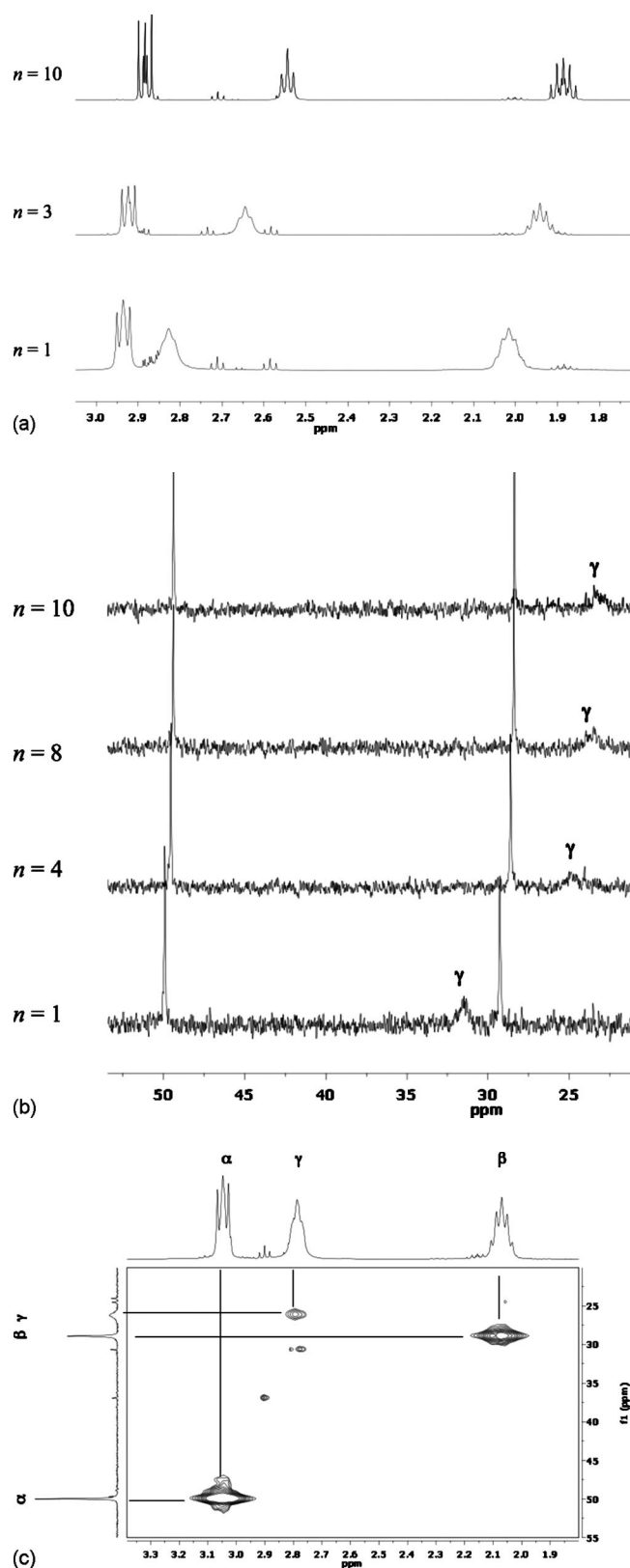


Figure 8. (a) Proton NMR spectra of $\text{CuCl} + n\text{MPS}$ in 0.25 M D_2SO_4 . (b) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of $\text{CuCl} + n\text{MPS}$ in 0.25 M D_2SO_4 . (c) ^1H - ^{13}C *gHMQC* spectrum of $\text{CuCl} + 3\text{MPS}$ in 0.25 M D_2SO_4 .

released protons also revealed around 90% reaction completion. Proton NMR peak integration of the SPS versus Cu-thiolate/MPS resonances in D_2O produced a mole ratio of 0.62. A 1:3 CuCl_2 :MPS

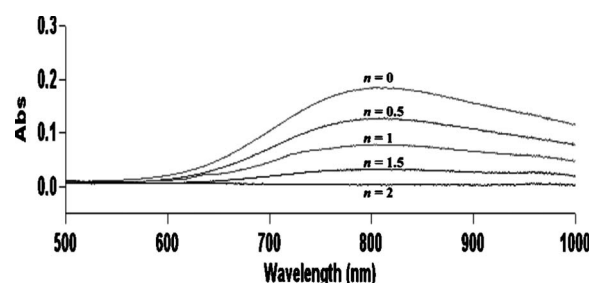


Figure 9. Electronic spectra of $\text{CuCl}_2 + n\text{MPS}$ in the visible region.

stoichiometry led to the release of 2.2 equiv of protons, consistent with the formation of higher order Cu(I)-thiolate species. Proton NMR peak integration gave an SPS to Cu-thiolate/MPS mole ratio of 0.5, indicating essentially complete Cu(II) reduction.

Cupric chloride and SPS.— Although no interaction between Cu(II) and SPS in acidic solution was expected, the existence of solid-state Cu(II)-disulfide bonding has been verified in several x-ray structures.²³⁻²⁷ We therefore examined the possibility of such interactions in solution. As confirmed by UV-vis spectroscopy, no color change was observed upon mixing an aqueous solution of CuCl_2 with 1 or more equiv of SPS. A broadened proton NMR spectrum of SPS was obtained along with reasonably sharp C-13 resonances, none significantly shifted from parent SPS values. Thus, we conclude that no chemical reaction between Cu(II) and SPS can be detected under our reaction conditions.

Conclusion

(1) In 0.25 M D_2SO_4 aqueous solution, SPS reacts directly with CuCl in a redox reaction to give a Cu(I)-thiolate product and Cu(II) with an equilibrium constant K_2 of $5.2 \times 10^{-3} \text{ M}^{-1}$. No evidence for formation of a Cu(I)-SPS or CuCl -SPS complex was found.

(2) In a similar solution, a less than stoichiometric amount of MPS with CuCl yielded an identical Cu(I)-thiolate product. Stoichiometric or excess MPS led to Cu(I)-thiolate species in exchange with free MPS. Assay of protons released from this reaction in aqueous solution revealed that thiolate complexation was incomplete until 2 equiv of MPS were added. Formation of higher order Cu(I)-thiolate products with excess MPS can also be inferred.

(3) As confirmed by NMR spectroscopy, the redox reaction of CuCl_2 with MPS yielded similar Cu(I)-thiolates together with SPS. In aqueous solution, potentiometric titration and UV-vis spectral data support 90% reaction completion at a 1:2 stoichiometry of CuCl_2 :MPS with formation of higher order Cu(I)-thiolates when excess MPS was present.

(4) No detectable interaction between CuCl_2 and SPS was observed in aqueous solution.

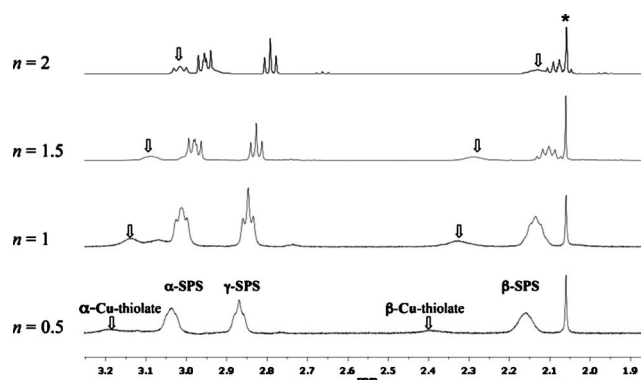


Figure 10. Proton NMR spectra of $\text{CuCl}_2 + n\text{MPS}$ in 0.25 M D_2SO_4 .

(5) The observed NMR spectral data supporting exchange between Cu(I), MPS, and Cu(I)-thiolate suggest a mode of activity for an accelerant whereby it can rapidly bind and exchange solution Cu(I) cations. The major findings in this report are based on solution spectroscopic data and on samples at accelerant concentrations (1–100 mM) substantially higher than in actual electroplating solutions. Although we consider these results to be of relevance to an improved understanding of fundamental accelerant solution chemistry, identification of similar chemical species on or near copper electrode surfaces during copper electroplating remains to be verified.

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