2080 Inorg. Chem. 1998, 37, 2080−2082

A New Synthesis of Tetrathiooxalate and Its Conversion to $C_3S_5^{2-}$ and $C_4S_6^{2-}$

Jonathan G. Breitzer, Jun-Hong Chou, and Thomas B. Rauchfuss*

School of Chemical Sciences and the Frederick Seitz
Materials Research Laboratory, University of Illinois at
Urbana-Champaign, Urbana, Illinois 61801

Received October 21, 1997

Introduction

The synthesis of tetrathiooxalate (tto^{2-}) is accomplished by the electrochemical reduction of CS_2 over a liquid mercury cathode in the presence of a quaternary ammonium or phosphonium salt (eq 1).[1] As recounted by Hoyer,[2] attempted

$$2CS_2 \xrightarrow[\text{Et}_4\text{NCl}]{\text{2 V vs NHE}} (Et_4N)_2C_2S_4 \qquad (1)$$

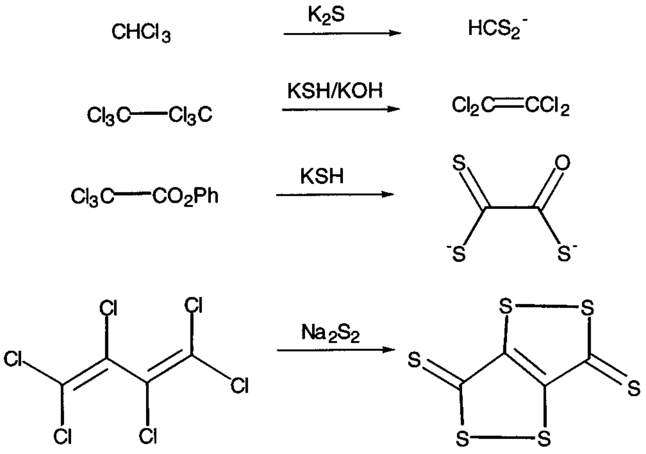
syntheses of tto^{2-} by the alkali metal reduction of CS_2 results in formation of $C_3S_5^{2-}$ according to eq 2.[3] Using electrochemi-

$$4Na + 4CS_2 \rightarrow Na_2CS_3 + Na_2C_3S_5 \qquad (2)$$

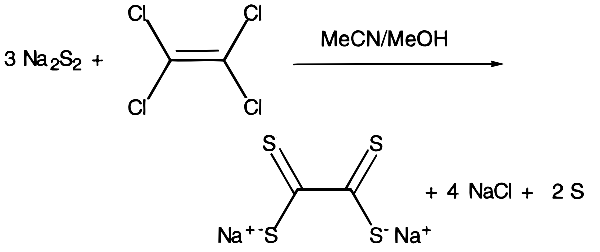
cally produced tto^{2-}, Reynolds and co-workers have synthesized several polymeric and oligomeric tto complexes, some of which are excellent electrical conductors.[4] Other C_2S_4 complexes are known but these are usually prepared by the reductive coupling of CS_2 with low-valent-metal complexes, e.g. $Cp_2Ti(CO)_2$.[5] Such complexes are not true sources of the free tto^{2-} moiety. Furthermore, it appears that many such compounds are best described as complexes of ethylenetetrathiolate, $C_2S_4^{4-}$. An intriguing but inefficient chemical route to tto involves the reaction of $(Et_4N)_2S_5$ with refluxing MeCN. A plausible intermediate in this process, dithioacetate ($CH_3CS_2^-$), also reacts with the polysulfide salt to produce tto^{2-}.[6]

The lack of a convenient synthesis of tto^{2-} has limited study of this fundamental two-carbon building block.[7] The coordination chemistry of tto^{2-} also remains restricted in scope, despite the very intriguing results on its polymeric and oligomeric coordination compounds.[4,8] The fact that most tto complexes exhibit strong M···M interactions suggests that tto^{2-} would be a useful reagent in preparing multimetallic arrays, relevant to the prevailing interest in supramolecular chemistry, materials science, and catalysis. Given this background as well as our recent familiarity with the sulfidation of chlorocarbons,[9] we undertook the synthesis of tto^{2-} by sulfidation of tetrachloroethylene. Prior work on the reaction of chlorocarbons and inorganic sulfide sources is summarized in the Scheme 1.[10−12] The conversion of chlorocarbons to chlorine-free products using inexpensive reagents such as alkali metal sulfides might be of some interest for the detoxification of organochlorine compounds.[13]

Scheme 1



Results



(3)

Synthesis of Tetrathiooxalate. We found that tto^{2-} forms in good yield by the reaction of sodium persulfide with tetrachloroethylene in hot methanolic acetonitrile. The product was obtained as the methanol (but not ethanol)-soluble Et_4N^+ salt. The conversion of the olefin to tto^{2-} involves formal oxidation of the carbon compound. The oxidizing equivalents are provided in the form of the persulfide anion S_2^{2-} (eq 3). In practice, we found that the reaction of C_2Cl_4 with 2 equiv of Na_2S_2 was more efficient than that using a mixture of Na_2S and Na_2S_2, as might be expected on the basis of stoichiometry of the reaction. We confirmed that tto^{2-} does not react with C_2Cl_4 under the conditions used for the synthesis of tto^{2-}. An occasional difficulty in our tto^{2-} synthesis arises from contamination of the $(Et_4N)_2$tto with NaCl, which was removed by

---

(1) (a) Jeroschewski, P. *Z. Chem.* **1981**, *21*, 412. (b) A review: Jeroschewski, P.; Hansen, P. *Sulfur Rep.* **1986**, *7*, 1.

(2) Hoyer, E. *Comments Inorg. Chem.* **1983**, *2*, 261.

(3) Reviews of $C_3S_5^{2-}$ chemistry: Olk, R.-M.; Olk, B.; Dietzsch, W.; Kirmse, R.; Hoyer, E. *Coord. Chem. Rev.* **1992**, *117*, 99. Svenstrup, N. B.; Becher, J. *Synthesis* **1995**, 215.

(4) Pullen, A. E.; Zeltner, S.; Olk, R.-M.; Hoyer, E.; Abboud, K. A.; Reynolds, J. R. *Inorg. Chem.* **1997**, *36*, 4163. Piotraschke, J.; Pullen, A. E.; Abboud, K. A.; Reynolds, J. R. *Inorg. Chem.* **1995**, *34*, 4011. Pullen, A. E.; Zeltner, S.; Olk, R.-M.; Hoyer, E.; Abboud, K. A.; Reynolds, J. R. *Inorg. Chem.* **1996**, *35*, 4420.

(5) Harris, H. A.; Rae, A. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1987**, *109*, 4739. Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M.; Zanello, P. *J. Am. Chem. Soc.* **1987**, *109*, 185.

(6) Bacher, A. D.; Sens, I.; Müller, U. *Z. Naturforsch.* **1991**, *47B*, 702.

(7) For a review of the older literature, see: Gattow, G.; Behrendt, W. *Carbon Sulfides and Their Inorganic and Complex Chemistry*; G. Thieme: Stuttgart, Germany, 1977.

(8) Strauch, P.; Dietzsch, W.; Hoyer, E. *Z. Chem.* **1983**, *23*, 448.

(9) Chou, J.-H.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1997**, *119*, 4537. Chou, J.-H.; Rauchfuss, T. B. *Z. Naturforsch.*, in press.

(10) Reuter, U.; Gattow, G. *Z. Anorg. Allg. Chem.* **1976**, *421*, 143. Engler, R.; Gattow, G.; Dräger, M. *Z. Anorg. Allg. Chem.* **1972**, *388*, 229.

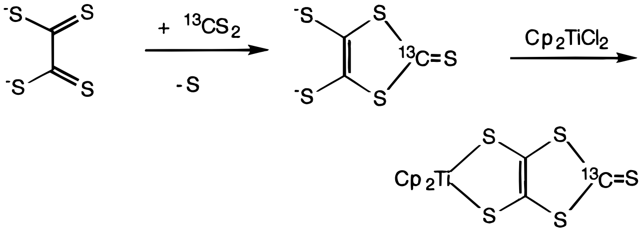
(11) Richter, A. M.; Fanghänel, E. *Sulfur Lett.* **1985**, *3*, 25.

(12) Stork, W.; Mattes, R. *Angew Chem., Int. Ed. Engl.* **1975**, *14*, 436 (*Angew. Chem.* **1975**, *87*, 452).

(13) *Bioremediation of Chlorinated Solvents*; Hinchee, R. E., Leeson, A., Semprini, L., Eds; Battelle Press: Columbus, OH, 1995.

S0020-1669(97)01327-X CCC: $15.00

Scheme 2



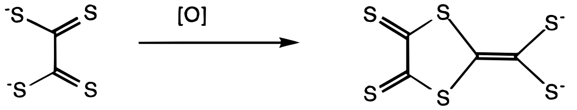
recrystallization from MeCN. Overall, the requirement for anhydrous Na_2S_2 is the chief disadvantage of this preparation; this salt can, however, be easily prepared on a 20 g scale via the direct reaction of Na and elemental sulfur in anhydrous ammonia.

We also synthesized tto^{2-} using hydrated Na_2S_2, prepared in situ from elemental sulfur and commercially available hydrated sodium sulfide ("$Na_2S{\cdot}9H_2O$") in methanol. This convenient method can be used to prepare $(NEt_4)_2$tto on a gram scale in a few hours using routinely available reagents, although the yields are slightly lower than those with the anhydrous route. In these experiments, we found that the rate of sulfidation increased with an excess of C_2Cl_4. It was also found that prolonged reaction times resulted in diminished yields. We confirmed that tto^{2-} is stable to anhydrous NH_3 (2 h at 0 °C—i.e., 48 psig). Subsequent experiments showed that Na_2S_2 and C_2Cl_4 react slowly in anhydrous ammonia to give small amounts of tto^{2-}.

The $(Et_4N)_2$tto was identified by microanalysis and by its IR and UV−vis spectra. The ^{13}C NMR chemical shift of a CD_3OD solution of $(Et_4N)_2$tto is δ 268.2, vs 268.7 observed for an aqueous solution.[1b] Methanolic $(Et_4N)_2$tto reacts with aqueous $Ni(H_2O)_6Cl_2$ to produce a black solid with approximate formula NiC_2S_4, with the appropriate IR spectrum.[14]

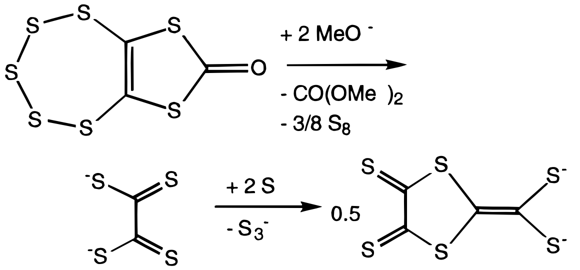
Conversion of tto^{2-} into $C_3S_5^{2-}$. It has long been proposed[1,2] that tto^{2-} is the precursor to $C_3S_5^{2-}$ in the reduction (chemical and electrochemical) of CS_2.[15] We confirmed this proposal by treating a DMF solution of $(Et_4N)_2$tto with CS_2 to produce $C_3S_5^{2-}$, which was spectroscopically identical to that generated by base hydrolysis of the bis(thioester) $C_3S_5(C(O)Ph)_2$.[3] The spectroscopic yield was virtually quantitative. Furthermore, we conducted this reaction using $^{13}CS_2$, trapping the product as the titanocene derivative.[16] The compound $Cp_2TiC_3S_5$ has rather distinctive optical and NMR properties; thus this experiment further confirms the conversion of tto^{2-} into $C_3S_5^{2-}$. The ^{13}C NMR spectrum of this species showed that the label was in the thiocarbonyl, i.e., $Cp_2TiS_2C_2S_2{}^{13}CS$ (Scheme 2).

Conversion of tto^{2-} into $C_4S_6^{2-}$. Prolonged reactions of C_2Cl_4 with Na_2S_2 result in dark solutions which were shown by UV−vis spectroscopy to contain $C_4S_6^{2-}$.[17] We hypothesize that this transformation involves oxidation of tto^{2-} by the small amount of sulfur generated (see eq 3). The reactivity of preformed tto^{2-} toward elemental sulfur was confirmed; this reaction cleanly gives $C_4S_6^{2-}$. This oxidative nature of this pathway is further indicated by the finding that treatment of tto^{2-} with 0.5 equiv of I_2 followed by heating gave blue $C_4S_6^{2-}$ in quantitative yield (eq 4). This coupling process may involve the intermediacy of the disulfide $(C_2S_4)_2^{2-}$.



(4)

Collectively, the above experiments on the oxidation of tto^{2-} provided the basis for an efficient synthesis of $C_4S_6^{2-}$, which is a binucleating ligand.[17] A mixture of C_2Cl_4 and Na_2S_2 in refluxing MeCN solution gives $(Et_4N)_2C_4S_6$ in 90% yield. The previous synthesis of $C_4S_6^{2-}$ requires the slow base hydrolysis of the bicyclic species C_3S_7O, itself obtained in two steps from $C_3S_5^{2-}$.[17] The present results suggest that the conversion of C_3S_7O into $C_4S_6^{2-}$ proceeds via the intermediacy of tto^{2-}, which, as discussed above, is highly susceptible to oxidation by elemental sulfur (eq 5).



(5)

Summary

A new route to tto^{2-} has been developed. Reactivity studies show that this species is an intermediate in the formation of two important thioanions, $C_3S_5^{2-}$ and $C_4S_6^{2-}$. The new syntheses of tto^{2-} and $C_4S_6^{2-}$ should facilitate further research on these binucleating ligands.

Experimental Section

Materials and Methods. Na_2S_2 was prepared by the addition of 12.83 g of S_8 to 9.2 g of Na in NH_3 followed by evaporation. The resulting orange solid was stored in a nitrogen-filled glovebox; it was crushed into a fine powder before use. $^{13}CS_2$ (99.99% enrichment) was obtained from Cambidge Isotopes (Andover, MA) and was diluted with five volumes of unlabeled CS_2 prior to use. Unless otherwise noted, reactions and workups were conducted under an inert atmosphere using degassed solvents.

Synthesis of $(Et_4N)_2$tto from Anhydrous Na_2S_2. A 500-mL round-bottom flask was loaded with 1.1 g (0.01 mol) of Na_2S_2 inside a N_2-filled glovebox. Approximately 20 mL of MeOH was added to the flask to dissolve the Na_2S_2. The resulting orange-yellow solution was then diluted with 200 mL of MeCN, giving a green coloration, followed by 1.02 mL (0.01 mol) of C_2Cl_4. No color change or precipitation occurred upon the addition of the C_2Cl_4. The solution was heated at reflux for 45 min. The solution became dark brown concomitant with the appearance of a large amount of pale yellow precipitate. The hot slurry was treated with 1.1 g (0.0066 mol) of solid Et_4NCl, and the mixture was allowed to cool to room temperature. The solvent was removed under reduced pressure, and 30 mL of MeOH was added to extract the product from the bulk of the NaCl. The filtrate was treated with ~200 mL of Et_2O to precipitate the crude product as dark orange microcrystals. The precipitate was washed thoroughly with CH_2Cl_2 to removed an impurity of the blue salt $(Et_4N)_2C_4S_6$. The resulting solid was extracted with 150 mL of MeCN, and the extract was filtered and concentrated until the appearance of orange yellow crystals. A small amount of MeOH (~5 mL) was added to redissolve the crystals, and 200 mL of Et_2O was added to crystallize analytically pure $(Et_4N)_2$tto. Yield: 0.45 g (36%). IR (KBr), cm^{-1}: 2976 (m), 1456 (m), 1397 (m), 1308 (w), 1182 (m), 1129 (m), 988 (s), 798 (m), 760 (m), 740

---

[14] Reynolds, J. R.; Karasz, F. E.; Lillya, C. P.; Chien, J. C. W. *J. Chem. Soc., Chem. Commun.* **1985**, 268.

[15] Jeroschewski, in a review,[1b] also mentioned his otherwise unpublished finding that tto^{2-} and CS_2 react to give $C_3S_5^{2-}$.

[16] Yang, X.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1989**, *111*, 3465.

[17] Szczepura, L. F.; Galloway, C. P.; Zheng, Y.; Han, P.; Rheingold, A. L.; Wilson, S. R.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 5220 (*Angew. Chem.* **1995**, *107*, 2027).

(m). ^{13}C NMR (CD$_3$OD): δ 268.2. UV−vis [λ_{max}, nm (ϵ, M^{-1} cm^{-1})] (MeOH solution): 286 (6400), 342 (3500). Anal. Calcd for $C_{18}H_{40}N_2S_4$: C, 52.37; H, 9.77; N, 6.78. Found: C, 52.14; H, 9.75; N, 6.68.

Synthesis of (Et$_4$N)$_2$tto Using Na$_2$S·9H$_2$O. A large crystal of Na$_2$S·9H$_2$O was rinsed with acetone and then ground in a mortar and pestle. A portion of this white powder, 3.04 g (12.65 mmol), was dissolved in 16 mL of MeOH, and the solution was treated with 0.407 g (12.68 mmol S) of elemental sulfur. After 15 min, this yellow, slightly turbid mixture was diluted with 120 mL of MeCN, causing the solution part to turn green and a pale yellow, flocculent precipitate to form. Upon heating to 70 °C, the solution developed a deep green coloration and an orange semisolid appeared on the bottom of the flask. This mixture was treated with 1.13 mL (11.1 mmol) of C_2Cl_4. Traces of a fine, white precipitate were observed immediately. The mixture was maintained at 70 °C for 25 min. Over this period, more white solid was observed, the orange semisolid disappeared, and the solution became orange-brown. The mixture was quickly cooled to room temperature and treated with 1.42 g of Et$_4$NCl followed by removal of the solvents in vacuo. The brown residue was treated with 30 mL of MeOH, resulting in a brown solution and a white solid, which was removed by filtration. The filtrate was treated with 80 mL of Et$_2$O, giving a yellow precipitate. The solid was collected in the air, leaving a pale brown filtrate, which was discarded. The solid was washed with three 10 mL portions of CH$_2$Cl$_2$ to remove (Et$_4$N)$_2$(C$_4$S$_6$). To the residue was added 140 mL of MeCN in two portions, and the mixture was filtered to remove the white solid (NaCl). The brown solution was concentrated to 20 mL under reduced pressure, causing orange crystals to form. This slurry was diluted with 30 mL of Et$_2$O to give additional crystals, which were washed with CH$_2$Cl$_2$. Yield: 0.512 g, 29%. Anal. Calcd for $C_{18}H_{40}N_2S_4$: C, 52.37; H, 9.77; N, 6.79. Found: C, 51.98; H, 9.87; N, 6.73. The reaction time of 25 min is important: reaction times of 1 h caused approximately half of the (Et$_4$N)$_2$tto to be converted to (Et$_4$N)$_2$(C$_4$S$_6$).

Conversion of tto^{2-} to C$_3$S$_5$$^{2-}$. Under an atmosphere of purified nitrogen, 25.4 mg of (Et$_4$N)$_2$tto was dissolved in 50.0 mL of DMF. A 0.500 mL aliquot of this orange solution was diluted with DMF to 5.00 mL. This dilute solution was transferred to an airtight cuvette with a path length of 1 cm, and excess CS$_2$ (10.0 μL) was added. A change in color from yellow to red was complete within 3 h. The yield of $C_3S_5^{2-}$, based on tto^{2-}, was determined spectroscopically (see below) to be 97%. To determine the extinction coefficient of $C_3S_5^{2-}$, a standard solution was prepared as follows. To approximately 5 mL of a 2 M solution of sodium methoxide was added C$_3$S$_5$(COPh)$_2$ (24.9 mg, 6.12×10^{-5} mol). The resulting deep red solution was evaporated to dryness and 5.00 mL of degassed DMF added. Under anaerobic conditions, a 50-μL aliquot of the resulting deep blue solution was diluted to 5.00 mL, and the resulting pale blue solution was transferred to an airtight cuvette. Neutralizing the excess base with ammonium bromide (20 mg) caused the solution to turn red immediately (λ_{max} = 490 nm; ϵ = 4610 dm^3 mol^{-1} cm^{-1}).

Preparation of Cp$_2$Ti(C$_3$S$_5$) from (Et$_4$N)$_2$tto. A suspension of 0.255 g of a mixture of (Et$_4$N)$_2$tto and NaCl—determined spectroscopically to contain 74% (Et$_4$N)$_2$tto (0.46 mmol)—in 20 mL of MeCN was treated with 0.040 mL of 17% ^{13}C-enriched CS$_2$. After 17 h, the resulting orange solution was treated with 0.116 g (0.466 mmol) of Cp$_2$TiCl$_2$ to give, after 1 h, a green solution. The solvents were removed under reduced pressure. The residue was extracted with 8 mL of CH$_2$Cl$_2$, and the extract was purified by column chromatography (silica gel, 2.5 × 24 cm), eluting with CH$_2$Cl$_2$. The first (green) band was concentrated and diluted with pentane to give green microcrystals. Yield: 0.0878 g (45%, based on (Et$_4$N)$_2$tto). ^{1}H NMR (CD$_3$COCD$_3$, 500 MHz, 23 °C) δ 6.2 (br). ^{13}C NMR (CD$_3$COCD$_3$): δ 215.8.

Oxidation of (Et$_4$N)$_2$tto to (Et$_4$N)$_2$C$_4$S$_6$. To a solution of 0.21 g (0.5 mmol) of (Et$_4$N)$_2$tto in 30 mL of MeOH was added 0.064 g (0.25 mmol) of I$_2$. No color change was apparent until the solution was heated to reflux. After 30 min, the violet mixture was cooled to room temperature and filtered. Approximately 50 mL of Et$_2$O was added to precipitate dark blue microcrystals of (Et$_4$N)$_2$C$_4$S$_6$. Yield: 0.100 g (90%).

(Et$_4$N)$_2$C$_4$S$_6$. A 500-mL round-bottom flask was charged with 1.32 g (0.012 mol) of Na$_2$S$_2$ followed by 20 mL of MeOH and 200 mL of MeCN. The green solution was treated with 0.41 mL (0.00378 mol) of C$_2$Cl$_4$, resulting in no apparent change in color or homogeneity. The solution was heated at reflux (80−85 °C) for 24 h. During this time, the solution became dark blue. The warm solution was filtered (with the complete exclusion of air) to remove the pale yellow precipitate (presumed to be NaCl and S$_8$). The filtrate was treated with 0.84 g (0.002 mol) of Et$_4$NBr, allowed to cooled to room temperature, and then concentrated to dryness. The residue was extracted with 50 mL of MeCN, and the extract was filtered to remove NaBr and then diluted with ∼200 mL of Et$_2$O to precipitate blue microcrystals. Yield: 0.90 g (90%, based on C$_2$Cl$_4$). IR (KBr): 1182 cm^{-1} ($\nu_{C=S}$). UV−visible [λ_{max}, nm (ϵ, M^{-1} cm^{-1})] (CH$_3$CN solution): 240 (25 000), 340 (8500), 800 (13 000). Anal. Calcd for $C_{20}H_{40}N_2S_6$: C, 47.95; H, 8.05; N, 5.59. Found: C, 47.78; H, 8.10; N, 5.63.

Acknowledgment. This work was supported by the U.S. Department of Energy, Division of Materials Science, under Grant DEFG02-96ER45439 through the University of Illinois at Urbana-Champaign, Frederick Seitz Materials Research Laboratory. This research was also supported by the NSF. We thank G. Holloway for help with the tto^{2-} preparation.

IC971327C