# Silver(I) Chemistry in Aqueous Alkaline Media. 2.[1] Study of the Interaction of Silver(I) with β-Disulfone Carbanions in Aqueous Alkaline Media

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Abstract: A study of the solubility and chemistry of silver(I) in the presence of β-disulfone carbanions in aqueous alkaline media is reported. It is found that secondary β-disulfone carbanion (**1a**) forms a much more alkali-soluble silver(I) complex than tertiary β-disulfone carbanions (**1b** and **1c**). Furthermore, the **1a** silver(I) complex is alkali soluble at much lower pH (9–12.5) than the complexes of **1b** and **1c**. The silver solvent efficiency (SSE), a concept that is developed to describe the silver halide solubilizing power of ligands in aqueous alkaline media, of **1a** suggests that even a 2 mol of Ag/1 mol of **1a** silver(I) complex is soluble in alkali. The structure and bonding of the complex of **1a** with silver(I) is studied. The first well-characterized example of an sp³ hybridized carbon bonded to silver(I) in a largely covalent linear bond is found for these complexes. It is concluded that the unique SSE of disulfones is related to Ag–C bonding in the complex, and the interrelationship between the two is discussed.

The dissolution and diffusion transfer of alkali-soluble silver(I) complexes are fundamental properties of most instant black and white photographic processes. Until recently, very little was known about the chemistry and bonding of silver(I) with heteroorganic anions in aqueous alkaline media. In our first study on this topic we reported the interaction of uracil with silver(I) at very high pH.[1] In order to further our phenomenological understanding of why some silver (I) complexes dissolve in alkali and others don't, we presently report on another series of anions that exhibit silver halide solubilizing properties in alkali. The stereochemistry of β-disulfone carbanions has been reported by Corey.[2] For example, the structure of the monoanion of 1,3-dithiane 1,1,3,3-tetraoxide (DTT, **1a**), has been determined by X-ray crystallography to
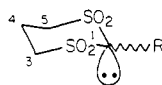
1a, R = H
1b, R = CH₃
1c, R = CH₃CH₂

contain an sp³-hybridized carbanion. It has been found for these anions "that carbanion stabilization by 3d orbitals has conformational and configurational dependencies that are less important than electrostatic and solvation effects". This indicates that resonance stabilization of the monoanion **1a**, for example, is minimal and that the amount of negative charge delocalized to oxygen is low. These observations led us to the present study of the interaction of β-disulfone carbanions with silver(I).[3] Our concerns were the following: (1) How do the solubilities of these complexes vary with pH? (2) What is the structure and bonding of the silver(I) complex of these anions? (3) What insight can be gleaned from the answers to these questions to further our general understanding of silver halide dissolution in aqueous alkali by heteroorganic anions?

Results

(A) Solubility and Stability of β-Disulfone Carbanion Silver Complexes. The equilibria that are important when considering the interaction of silver(I) with disulfone carbanions in dilute aqueous alkaline media are shown in Table I. (These mea-

surements were carried out for very dilute solutions to limit the formation of oligomeric species. NMR data (vide infra) for concentrated solutions indicate that oligomerization does occur at higher concentrations.) The log K values for eq 1, 2, and 3 are taken or derived from literature values.[4] The formation constants for $Ag(1)_2^- \equiv 3$ and $Ag(OH)(1)^- \equiv 2$ have been determined by the method previously described.[1,4] Equations 1, 4, and 5 have been combined to give eq 6 and 7. Equations 6 and 7 give the dissolution of AgBr via complexation. For example, the log K observed for eq 6 shows that the concentration of solubilized silver bromide occurs in the order **1a** ≫ **1c** > **1b**. The pK_a of DTT has been determined to be 12.6.[2a,c]

Figures 1 and 2 show the data obtained for the solubilization of AgBr vs. pH for the disulfones **1a–c**. It is evident that all three ligands increase the solubility of AgBr in alkali in the range 12.5–14.5. However, the unsubstituted ligand (**1a**) is by far the most effective in this property. Variation of the concentration of the ligand had little effect on the solubility curves of the three ligands. At pH 10–12.5 **1a** is the only one of the three ligands that dissolves AgBr. Figure 3 is a plot of the total moles of silver dissolved per mole of ligand vs. pH. We designate this plot as a measure of the silver solvent efficiency (SSE) of a given ligand. The data show that only in the case of DTT is the SSE above 1 (at pH 14.5; SSE ~1.7).

The disulfone DTT and the isolated 1 mol/1 mol of Ag(I) (mole/mole) complex **2** have contrasting solubilities. The disulfone is virtually insoluble in water. As the pH of the solvent increases, the solubility of **1a** also increases. In 2 M KOH it is soluble up to 0.14 M. It is soluble up to 0.03 M in 0.1 M KOH and is insoluble in 7.9 M KOH. Thus, the solubility of the disulfone is not very high and it is confined to a small range of pH values. Alternatively, the isolated complex **2** is soluble in water up to 0.3 M. Its solubility decreases as the basicity of the solvent increases. For example, in .01 M KOH the solubility of **2** is much less than 0.3 M. When **2** is isolated, dissolved in water and titrated with nitric acid, 2 equiv of acid are consumed per mole of complex. The precipitated solid obtained from this acidification is pure DTT. The first equivalence point of this titration is ca. 11.7 pH. It is evident, therefore, that bonding of silver in the complex has lowered the apparent pK_{a_2} of DTT (vide infra).

(B) Structure and Bonding of β-Disulfone–Silver(I) Complexes. NMR Data. The C-13 and H-1 NMR data for DTT in alkali alone and in the presence of Ag(I) under a variety of conditions are shown in Table II. C-13 NMR spectra of the 0.3 M

(1) For part 1 in this series see: J. R. DeMember and F. A. Wallace, *J. Am. Chem. Soc.*, **97**, 6240 (1975).
(2) (a) E. J. Corey, H. Konig, and T. H. Lowry, *Tetrahedron Lett.*, 1962, 515; (b) D. J. Cram, "*Fundamentals of Carbanion Chemistry*", Academic Press, New York, 1965, 71–84 and references therein; (c) R. P. Bell and B. G. Cox, *J. Chem. Soc. B*, 652 (1971).
(3) R. B. Greenwald, U.S. Patent 3 958 992, 1976.

(4) (a) F. A. Cotton and C. Wilkinson, "Advanced Physical Chemistry", Interscience, New York, 1966; (b) L. D. Sillen and A. F. Martell, "Stability Constants of Metal Ion Complexes", Metcalfe and Cooper Ltd., London, 1964.

Table I

	log K			eq
$AgBr(s) + OH^-(aq) \rightleftharpoons \frac{1}{2}Ag_2O(s) + \frac{1}{2}H_2O + Br^-$	-12.30			1
$\frac{1}{2}Ag_2O(s) + \frac{1}{2}H_2O + OH^- \rightleftharpoons Ag(OH)_2^-$	3.82			2
$\frac{1}{2}Ag_2O(s) + \frac{1}{2}H_2O \rightleftharpoons AgOH$	5.75			3

	1a	1b	1c	eq
$\frac{1}{2}Ag_2O(s) + \frac{1}{2}H_2O + 2(1)^- \rightleftharpoons Ag(1)_2^- + OH^-$	8.9	2.8	3.4	4
$\frac{1}{2}Ag_2O(s) + \frac{1}{2}H_2O + (1)^- \rightleftharpoons Ag(OH)(1)^- \cong 2$	4.1	-0.2	0.6	5
$AgBr(s) + 2(1)^- \rightleftharpoons Ag(1)_2^- + Br^-$	3.4	-9.2	-8.9	6
$AgBr(s) + (1)^- + OH^- \rightleftharpoons Ag(OH)(1)^- + Br^-$	-8.2	-12.5	-11.5	7
$2AgBr + (1)^- + 2OH^- \rightleftharpoons Ag_2(1)(OH)_2^{2-} + 2Br^-$	undetermined			8

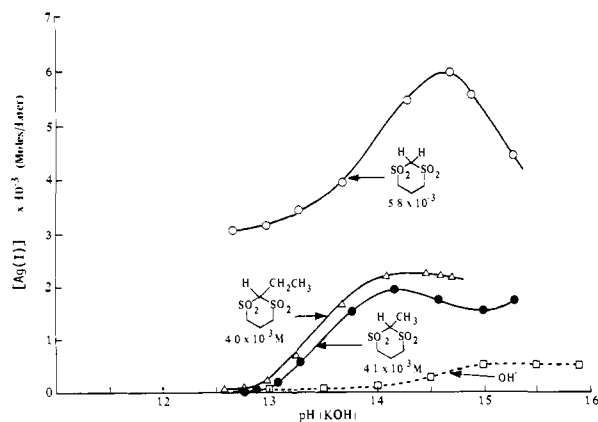**Figure 1.** Solubilization of AgBr vs. pH for disulfones **1a-c**.
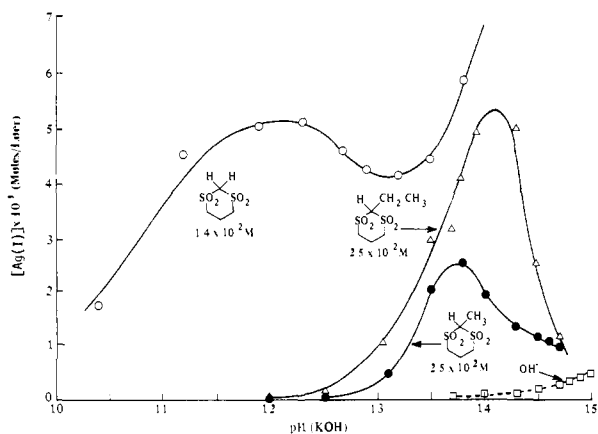
Figure 2. Solubilization of AgBr vs. pH for disulfones **1a-c**.

Figure 3. Silver solvent efficiency (SSE) for disulfones **1a-c** vs. pH in KOH.
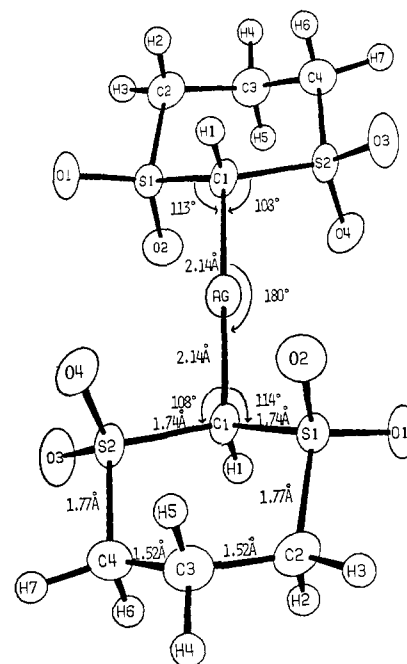
Figure 4. Detailed structure of the 2 mol of DTT/mol of Ag complex, **3**, from X-ray crystallographic data.

(mole/mole) complex are shown in Figures 5 and 6. The C-13 NMR signals for the C1 carbon atoms of the mole/mole complex in Figure 5 appear at 73.2, 71, and 75 ppm respectively as a triplet (J_{AgC} = 103 Hz) of triplets (J_{AgCAgC} = 6.1 Hz) superimposed upon two broad multiplets. The signals for C3,5 and C4 of the mole/mole complex are shown in Figure 6 as two singlets in the 50-ppm region and two singlets in the 20-ppm region, respectively. It is evident from the spectra in Figures 5 and 6 that there are two major structural isomers present in highly alkaline solutions of the mole/mole complex. The data in Table II show that the relative concentration ratio of these two species is a function of the concentration of the mole/mole complex, the pH of the solution, and the relative amount of excess Ag(I) available in the preparation. The relative C-13 NMR line intensities of the resolved triplet of triplets for C1 at 73.2 ppm and the resolved upfield singlets at 50 ppm for C3,5 and 19 ppm for C4 are reduced as the concentration of DTT/Ag(I) goes up. It appears that the concentration of the isomer yielding these C-13 NMR lines is reduced to only 5% when a 2-fold excess of Ag(I) is present in the parent solution of the complex. At higher concentrations of the mole/mole complex and when excess Ag(I) is present a single broad triplet resonance ($J \approx 100$ Hz) is observed for C1, and the broader lines for C3,5 at 52 ppm and C4 at 20 ppm are enriched
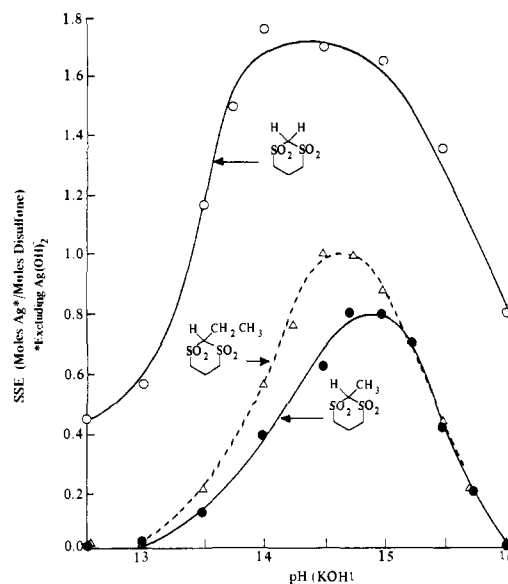
at the expense of the more resolved lines at 50 and 19 ppm. These data are best explained by the equilibria shown below in eq 9-12 (Scheme I) for concentrated solutions of the mole/mole complex in aqueous alkaline media. As shown in eq 11 the internal attack of the carbanion end group in **5** where m = 2 competes effectively with OH$^-$ to yield species **6**, which gives the relatively highly

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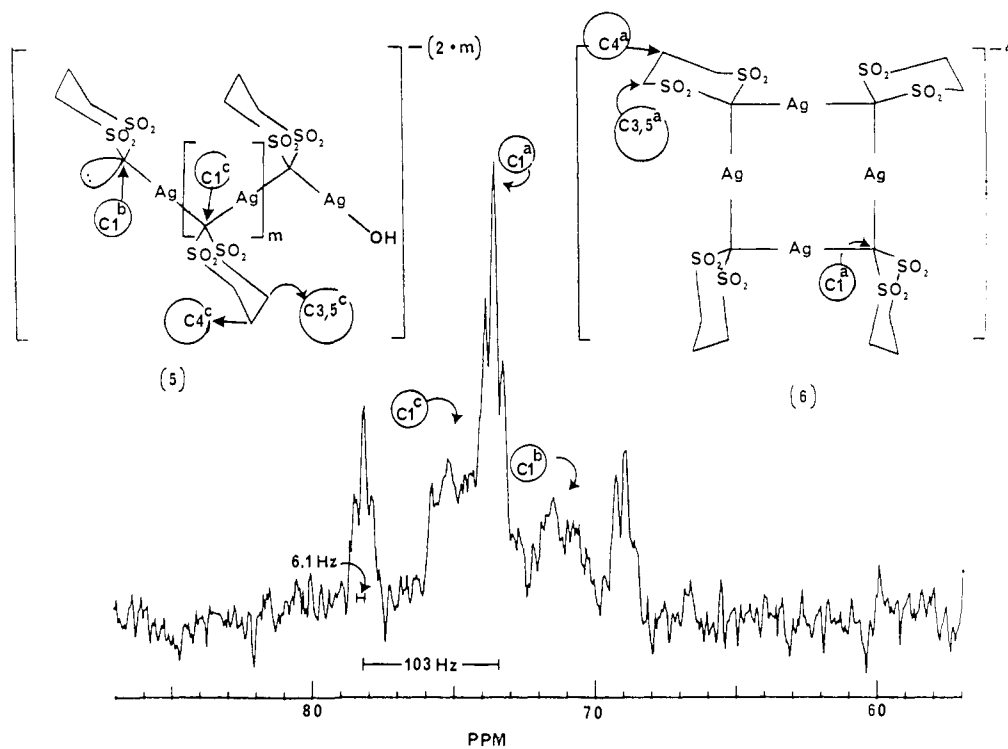*J. Am. Chem. Soc., Vol. 105, No. 17, 1983* 5649

Figure 5. C-13 NMR spectrum of the C1 carbon atom of the 0.3 M mole/mole complex in 2 M KOD, D_2O at 25 °C sample temperature.
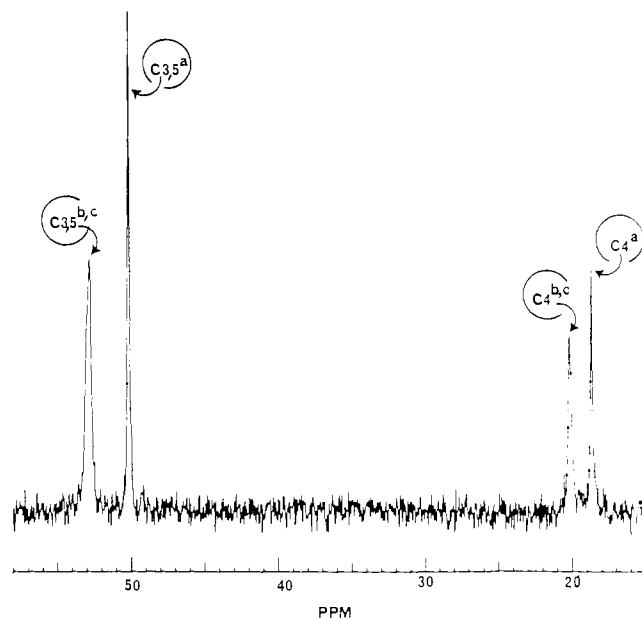
Figure 6. C-13 NMR spectrum of the C4 and C3,5 carbon atoms of the 0.3 M mole/mole complex in 2 M KOH, H_2O at 25 °C sample temperature.
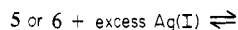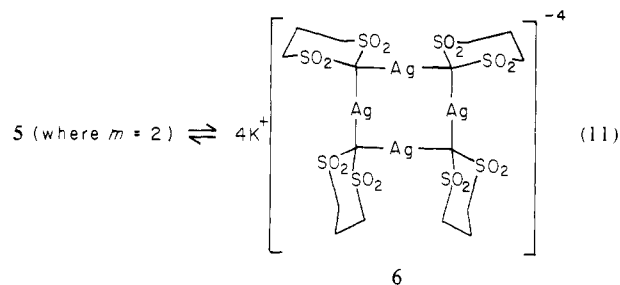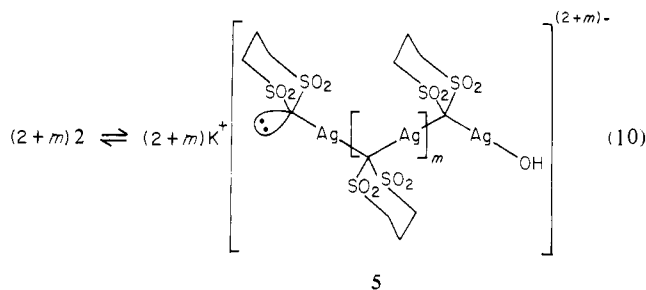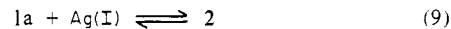
resolved triplet of triplets for C1 shown in Figure 5 as spectrum C1ᵃ. The carbanion end group in **5** is assigned to the broad C-13 NMR multiplet at 71 ppm (spectrum C1ᵇ in Figure 5). The broadness in this resonance is consistent with the variations in the chain length of this low molecular weight oligomer (i.e., multiple chemical shifts) and to various differing conformational arrangements possible for this open-chain species. These differences lead also to the broad multiplet at 75 ppm (spectrum C1ᶜ in Figure 5) for the repeat and second end group in oligomer **5**. The C-13 NMR signals for the C4 and C3,5 carbons are also assigned for these two structures as shown in Figure 6. When an excess of Ag(I) is available, the formation of oligomer **5b**, where the carbanion end group reacts with excess Ag(I), leads to a shift in equilibria in these solutions from species **5** and **6** to **5b** as shown in eq 12. A single broad C-13 NMR triplet is observed for the

Scheme I

$$1a + Ag(I) \rightleftharpoons 2 \qquad (9)$$

$$(2+m)2 \rightleftharpoons (2+m)K^+ \qquad (10)$$

5

$$5 \text{ (where } m = 2) \rightleftharpoons 4K^+ \qquad (11)$$

6

5 or 6 + excess Ag(I) $\rightleftharpoons$

$$(2+m)K^+ \qquad (12)$$

5b
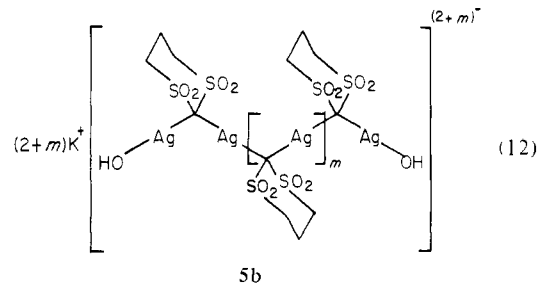
C1 carbon of all groups in species **5b**.

The C-13 NMR spectra of water and Me_2SO-d_6 solutions of the single species **2**, which is isolated by methanol precipitation

Table II. NMR Spectroscopic Data for DTT and Silver(I)

composition	compd (% mol/mol)	medium	chemical shift, δ^b [multiplicity, Hz]^c					
			C1	C3,5	C4	H1	H3,5	H4
DTT		Me$_2$SO-d_6	70.1 (2.5)^b	49.9 (-1.2)	17.3 (-2.0)	5.20	3.35	2.30
DTT		2 M KOH, H$_2$O^d	67.6	51.1	19.3			
0.3 M Ag(I)	6 (47)^e	2 M KOH, H$_2$O^f	73.2 (5.6) [t, J_{CAg} = 103; t, J_{CAgCAg} = 6.1]	50.1 (-1.0)	18.7 (-0.6)			
0.3 M DTT	5 (53)		71, 74.5	53.1 (2.0)	20.4 (1.1)			
0.6 M Ag(I)	6 (27)^e	2 M KOH, H$_2$O	[masked]	50.5 (-0.6)	18.9 (-0.4)			
0.6 M DTT	5 (73)		73.8 (6.2) [br t, J_{CAg} = 103]	53.2 (2.1)	20.4 (1.1)			
supernate								
0.6 M Ag(I)^c	6 (5)^e	2 M KOH, H$_2$O	[masked]	50.6 (-0.5)	19.0 (-0.3)			
0.3 M DTT	5b (95)		73.8 (6.2) [br t, J_{CAg} = 103]	53.3 (2.2)	20.5 (1.2)			
	2	10% in H$_2$O	74.0 (6.4) [br s]^h	52.4 (1.3)	19.6 (0.3)			
	2	5% in Me$_2$SO-d_6	74.0 (6.4) [br s]^h	52.1 (1.0)	19.8 (0.5)	i	3.40	2.50

^{a} Chemical shifts are reported in ppm down field (+) of tetramethylsilane. ^{b} $\Delta\delta = [\delta - \delta DTT^-]$. ^{c} Silver-109–carbon-13 coupling constants (t = triplet) are reported for the complexes with the bond separation expressed as a subscript. ^{d} The pKa of DTT is 12.61 and in 2 M KOH it should be 90% monoanion. ^{e} The relative quantities of oligomer 5 and cyclic quatramer 6 were determined by C-13 NMR integration of the C3,5 peaks for each sample. ^{f} This C-13 NMR spectrum is shown in Figures 5 and 6. ^{g} The sample was run as a supernate decanted from excess Ag$_2$O solid. ^{h} Although the chemical shift for C1 in 2 indicates Ag–C bonding, no discernable Ag–C coupling is observed for the isolated complex. Since it is not soluble in solvents where the temperature can be lowered, no low-temperature studies were possible. ^{i} No signal for the C1-H proton in 2 could be observed under the conditions permitted by the limiting solubility of this salt in only water and Me$_2$SO.

from the mole/mole complex in alkaline solution, are tabulated in Table II. It appears that equilibrium processes lead to a loss of C–Ag coupling for the carbons of the ligand in 2. However, the C-13 NMR shift for C1 in 2 at 74 ppm in both solvents is consistent with Ag–Cl bonding in the complex. The vapor-pressure osmometry data for 2 described below show that the oligomers 5, 6, and 5b, which form in alkaline solutions of DTT and Ag(I), do not form in water solutions of 2. Since the complex 2 is only soluble in solvents that freeze at moderately high temperatures, we were not able to freeze out any equilibria to help characterize the equilibrium chemistry of the complex 2.

Complex 3 is not appreciably soluble in alkali, water, or solvents so that C-13 NMR spectra were not obtained for this compound. It should be noted that complex 3 often precipitates from alkaline solutions of the mole/mole complex and in preparing solutions of complex oligomers 5, 6, and 5b it is best to add the solution of ligand to that of the Ag(I). This keeps Ag(I) in excess during the mixing process and minimizes the tendency for complex 3 to precipitate.

The IR spectra of DTT and its isolated 2 and 3 silver(I) complexes show that the frequency of the absorption of the SO$_2$ groups is shifted to slightly lower energy in the complex: 1290 (SO$_2$ asymmetric) and 1140 (SO$_2$ symmetric) cm^{-1} for DTT and 1220 (-70) (SO$_2$ asymmetric) and 1094 (-46) (SO$_2$ symmetric) cm^{-1} for 2 DTT/1 Ag and 1 DTT/1 Ag. The region of the IR spectra (200–800 cm^{-1}) where Ag–O bonds in analogous compounds strongly absorb, is essentially devoid of any strong signals in these complexes.[5,6] A strong OH absorption band at 3300 cm^{-1} in the spectra of both complexes is consistent with the presence of associated water in the isolated complex crystal structure of both 2 and 3.

Elemental analyses of the isolated 2 and 3 complexes of DTT are consistent with their formulas being KAgC$_4$H$_8$S$_2$O$_5$ and KAgC$_8$H$_{16}$S$_4$O$_9$, respectively. The molecular weight of complex 2 was determined by vapor-pressure osmometry in water to be 354 ± 7 (calculated 347.1) g/mol. The molecular weight determination shows that the isolated complex 2 is not a dimer or oligomer in nonalkaline aqueous solution and also that polyionic associations in dilute nonalkaline solutions of 2 are minimal. This

is in contrast to the parent alkaline solutions of the mole/mole complex where the NMR data clearly indicate that oligomers are present.

Recrystallized complex 3 was studied by X-ray crystallographic analysis. From X-ray data (Figure 4), its overall molecular formula is K$^+$H$_2$OAg[(DTT)]$_2^-$, the same as that found by elemental analysis. Silver sits on an inversion center with a ligand on either side exactly at 180° and a silver–carbon bond distance of 2.147 Å. Potassium is also on an inversion center and is six-coordinate octahedral to within 5° to four oxygens from four disulfone moieties and two from water. Complex 2 was not stable and 3 was obtained upon recrystallization of 2 regardless of the ratio of ligand to silver in the preparation. Complex 2 was obtained by methanol precipitation from 1 mol/1 mol mixture of the ligand and AgNO$_3$.

Discussion

From the spectroscopic and elemental analysis data of the isolated complexes 2 and 3 and the X-ray crystallographic data of isolated complex 3, the structures of the complexes 2 and 3 are assigned as shown below. The important bond distances and bond
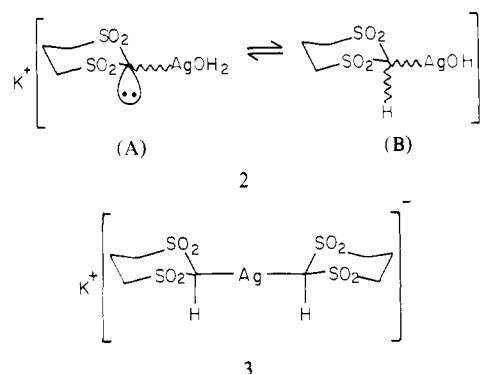

angles for the complex 3 as determined from X-ray crystallography are shown in Figure 4. Linear covalent bonds with nitrogen and sulfur ligands are known. These are reported to have bond lengths in the range 2.14–2.18 Å. Silver sp^3 carbon bonds have been postulated as intermediates in the thermolysis of *n*-alkylsilver(I) ate complexes.[7] In some instances low-temperature NMR spectra of these complexes have shown silver–carbon coupling ($J_{AgC} \sim$ 100 Hz) indicating silver–carbon bonding in the complex.[7j,k] To our knowledge, this is the first well-characterized example of silver stably bonded to an sp^3-hybridized carbon.[7] Furthermore, a linear

(5) A. H. M. Driessen-Fleur and W. L. Groeneveld, *Inorg. Chim. Acta*, **7**, 139 (1973), and references therein.

(6) (a) K. Tunaboylu and G. Schwarzenbach, *Hel. Chim. Acta*, **54**, 235 (1971); (b) H. Vahrenbamp, *Angew. Chem., Int. Engl., Ed.* **14**, 322 (1975); (c) C. D. M. Beverwljie, G. J. M. Van der Kerd, A. M. J. Leusink, and J. G. Noltes, *Organoment. Chem. Rev., Sect. A*, 215 (1970), and references therein.

Ag–C bond length of 2.14 Å suggests that it is largely covalent. However, these bonds are not so strong that they cannot be broken by acid to regenerate the ligand and free silver.

It is generally true that heteroorganic anions that are soluble in aqueous media are rendered less soluble when they are complexed with silver.[1,3,5] However, the solubility of complex **2** is greater than that of **1a** itself. Specifically, the maximum solubility of **1a** is 0.14 M in 2 M KOH whereas that of the isolated complex **2** in water is up to 0.3 M. The explanation for this is apparently related to the substantial lowering of the pK_{a1} (eq 13) of the C1–H

$$\text{(structure 4)} \xrightarrow{pK_{a1} \approx 11.7} \textbf{2} \qquad (13)$$

4
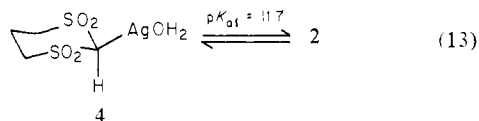
proton in compound **4** and the greater solubility of the complex monoanion **2** relative to **1a**. When **2** is titrated with nitric acid in water, the data suggest that the pK_{a1} **4** is ca. 11.7, whereas pK_{a1} DTT is 12.6. Thus, the effect of silver(I) at C1 is to somehow stabilize the carbanion at C1. Whether this is an inductive, mesomeric, or solvent effect or combination of these effects is not clear at present. Alternatively, it is apparent that the tautomerism of anion **2**, formed from the ionization of **4**, is likely to make the C1–H proton of compound **4** more acidic than the C1–H of DTT where no anion stabilizing tautomerism is available. The SSE (Figure 3) of DTT of ca. 1.7 suggests the presence of a substantial amount of compound **7** in dilute solutions of the ligand (see eq 4) where a second silver atom is bonded to C1 through a similar

$$\textbf{2} + \text{Ag}^+ \rightleftharpoons \text{K}_2^+ \left[\text{(structure 7)} \right]^{2-} \qquad (14)$$

7
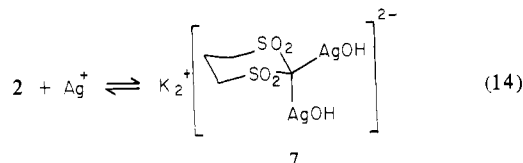
process as that described for the first silver ion. In more concentrated solutions the formation of oligomers **5**, **6**, and **5b** predominate.

It has been reported for uracil–silver(I) complexes[1] that "the effectiveness with which silver(I) is solubilized in aqueous KOH by such a ligand is related strongly to the solubility of the complex itself and not only to the strength of the silver–ligand bonding interaction". This concept applies here. Silver bromide solubilization is possible only when the solubility product of silver bromide is exceeded by a complex function of pH, pK_a, and the stability constants β_1 and β_2.[1,3] However, even if the above criterion is met, whether a precipitate or a soluble species forms depends on the charge to molecular weight ratio and on the solvation properties of the complex. DTT is an example where solubilization of AgBr is essentially related to the ionization of the second C1–H of **4** to give structures **2**, **5** and **6**. This leads to formation of species that have favorable electrostatic and solvation properties for solubilization in aqueous alkaline media since they have a high charge/mole weight ratio. These alkali soluble anions, **2,3,5,6**, and **5b**, react further with Ag(I) to form the alkali-soluble complex **7**. The situation for uracil and thiosulfate are similar. That is, the resulting species have a relatively high charge to molecular weight ratio. Thus, what the data suggest is that model systems for better silver halide solubilization go

beyond simply thinking of materials that will bind Ag(I) effectively in a complex.[8] For 2:1 complexes, the charge to molecular weight ratio can also be large enough to produce dissolution in alkaline media (eg., structures **3** and **7**) and similar arguments to those presented above would be applicable. In the case of DTT, and probably β-disulfones in general, the formation of the complexes such as **2–6** and especially **7** make it one of the most powerful heteroorganic silver halide dissolving reagents known for alkaline media.

Experimental Section

General. H-1 and C-13 NMR spectra were recorded on a Bruker 270-MHz NMR spectrometer at 30 °C probe temperature. The instrument was at the NMR Facility for Biomolecular Research, at the Francis Bitter National Magnet Laboratory, MIT, Cambridge, MA. The internal temperature of the samples varied from ca. 45 to 50 °C due to their conductivity. When a heat-sensitive solution was studied, it was cooled externally. Usually a solution temperature of 25 °C could be maintained with probe cooling to 18 °C for 2 M KOH. IR spectra were recorded on a Perkin-Elmer 580 spectrophotometer for KBr pellets. Molecular weights were determined in water by vapor-pressure osmometry on a Mechrolab Model 302 vapor-pressure Osmometer. A standard curve for dextrose was used and a value of 177 ± 7 g/mol was obtained for compound **2** potassium salt. This was compared with a standard curve for KCl where the observed value was 37.3, which is that expected for this ionic solution ([K] + [Cl]/2). Thus the correct value for the molecular weight of compound **2** is twice the observed value or 354 ± 7 g/mol. X-ray crystallographic analysis was carried out by Molecular Structure Corporation, College Station, TX. The details of the X-ray work are available upon request. EMF measurements were made with an Orion 801 meter using an Orion Research Silver Sulfide Sulfide electrode and an Orion Standard double-junction reference electrode. All EMF measurements were performed in the dark at constant ionic strength at 25 °C. All pH and pD values were calculated by Pitzer's equation.[9]

Compounds **1a–c** were synthesized by a procedure that has been described previously.[10] They were recrystallized several times to high purity as shown by melting point, mass spectra, and liquid chromatography. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN.

Determination of Stability Constants. The formation constants for silver(I) complexation with **1a–c** in 2 M KOH were determined as follows: Stock solutions of 5×10^{-3} M ligand in 2 M KOH were made by dissolving 2.5×10^{-3} mol each of 1a–c in 500-mL portions of 2 M KOH. Portions of the three solutions (50 mL each) were incrementally titrated with 0.050 82 N AgNO₃ (aqueous). The relative EMF was measured after each addition. Each addition was allowed approximately 5 min to equilibrate and each measurement was made without stirring. The β_1 and β_2 formation constants were extracted from the titration data with using a version of MINIQUAD,[11] a computer program.

Silver Solubility Measurements. The total solubilized silver bromide concentration was determined as follows. Equimolar mixtures of KBr and AgNO₃ were combined with enough solid disulfone to give formal concentrations of 10^{-4}, 10^{-3}, and 10^{-2} F of 1a–c disulfones when diluted with water. The AgNO₃ and KBr were at least a 100:1 excess in mole ratio over the disulfone. The solid mixtures were ground with a mortar and pestle to ensure homogeneity. Portions of the mixtures were each combined with 25-cm³ portions of KOH solution with molarities that varied in such a way that the pH's ranged from 10–16 as calculated by Pitzer's equation. A control was prepared in the same way as the samples except the disulfone was not added. The mixtures were shaken mechanically for 24 h to ensure equilibration.

The total dissolved silver(I) concentrations were measured by atomic absorption spectrometry. Each sample was first centrifuged for 10 min in a high-speed analytical centrifuge. One thousand microliter portions of the centrifugate were diluted to 25 cm³ in dilute CNI⁻ solution. CNI⁻ is a stabilizing agent for Ag⁺. These solutions were analyzed by AAS for total silver content.

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(8) Special cases such as uncharged macrocyclic ligands (see: J. Charkoudian, U. S. Patent 3 893 855, 1975) would not be subject to considerations such as charge/molecular weight since other factors determine solubility in this case (J. Charkoudian, U.S. Patent 3 883 350, 1975). Although there may be other exceptions, we believe this concept is applicable in the majority of cases.

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Preparation of Solutions of the Soluble Silver Complexes for NMR Analysis. (I) Equimolar, 2. To 0.5 cm³ of 2 M KOH was added 10 mg (0.054 mmol) of ligand. To this solution 0.54 cm³ of 0.1 N AgNO₃ (0.054 mmol) was added slowly with gentle stirring. The mixture was stirred until all of the Ag₂O formed dissolved. Precipitation of complex 3 sometimes occurs when this procedure is carried out. We found this could be prevented by the addition of the ligand to the silver solution. This clear, colorless solution was then added to a vigorously stirred solution of 100X absolute methanol. The resulting precipitate was washed with anhydrous methanol to neutral rinse, and the resulting solid was air dried: mp 220 °C dec. Anal. Calcd: C, 13.84, H, 2.32; S, 18.47; K, 11.26; Ag, 31.07. Found: C, 13.82; H 2.33; S, 18.39; K, 11.37; Ag, 30.92. The sample was kept in the dark to prevent silver photolysis.

(II) 2 mol of Ligand (DTT) to 1 mol of Silver, 3. The procedure for preparation of complex 3 was the same as that for 2 except that 0.28 cm³ of 0.1 N AgNO₃ (0.0272 mmol) was used in this case and that the precipitate of complex 3 forms immediately after the solution is prepared: mp 240 °C dec.

Preparation of Crystals for X-ray Analysis, 3. An approximately 4% solution of DTT in 2 M KOH was prepared by simple addition of these two reagents followed by rigorous agitation. If after mixing undissolved material was still present, the solution was filtered. With rigorous agitation a slightly less than stoichiometric quantity of aqueous silver nitrate was then added. Precipitation of white crystalline 3 occurred after approximately 1/2 – 2/3 of the silver nitrate had been added. In practice, addition of a stoichiometric amount of silver resulted in formation of a small amount of silver oxide that could not be dissolved by further agitation. This was evidenced from visual observation of the dark brown silver oxide precipitate. When this occurred incremental addition of the disulfone was necessary until all of the silver oxide had dissolved.

The white precipitate was then suction filtered onto a sintered glass frit and washed with methanol until the wash was neutral to litmus. It was then recrystallized from water. In a test tube a saturated aqueous solution of the silver–disulfone complex was prepared at steam temperature. If any undissolved materials were observed, the solution was hot filtered into a second test tube. To prevent premature crystallization, all work was performed on a steam cone. At this point the steam was gradually reduced to zero over a 15–20-min period. The solution was then allowed to set undisturbed overnight. The crystals obtained were gathered onto a sintered glass frit and washed several times with methanol and air dried: mp 245 °C dec.

Photochemistry of Acetone in Surfactant Solutions[1]

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Abstract: Acetone triplets, generated predominantly in the aqueous pseudophase, are extremely mobile probes in micellar solution. Their exit and entry rates exceed 10^8 s^{-1} and 10^{10} M^{-1} s^{-1}, respectively. Exit is competitive even with fast (diffusion controlled) intramicellar processes, such as exothermic triplet energy transfer. Photoreduction by the surfactant plays an important role in the absence of added quenchers. While acetone triplets can be readily studied, experiments with other aliphatic carbonyl compounds are complicated by short lifetimes owing to self-quenching (aldehydes) and Norrish Type I and Type II reactions. This may provide insight into the reasons for nature's choice of acetone triplet as a species of biological importance.

Flash techniques have become widely used in the study of organized systems; among these, micelles have received considerable attention. Studies of this type lead to information on the behavior of short-lived reaction intermediates,[2-9] solubilization of added reagents,[10] as well as the properties of the aggregate itself,[11,12] such as polarity, critical micelle concentration (cmc), and aggregation number.

This study of acetone in several micellar systems has been mainly motivated by two reasons. First, flash studies of this type usually involve photoexcitation in the micellar pseudophase; in the case of acetone, one can expect light absorption to occur predominantly in the aqueous phase. We thought it would be desirable to understand better the effect of excitation site on the photoprocesses which follow.

Second, triplet acetone has been established to be an important intermediate in biological systems,[13] where it can be generated thermally through oxidation processes, involving particularly the

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