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Oxide Salt Reactions in Matrix Isolation: Infrared Spectra of the $Tl^+{}_2SO_3{}^{2-}$ and $Tl^+{}_2S_2O_5{}^{2-}$ Triple Ions

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The oxide salt/molecule reaction technique, in which an ionic oxide-containing salt molecule is vaporized and codeposited with a Lewis acid, has been employed for the study of sulfur oxyanions. The reaction of Tl_2O with SO_2 under matrix isolation conditions has given rise to two distinct sets of product bands, the first of which was characterized by bands near 1086, 1067, 974, 588, 548, and 442 cm^{-1}. These absorptions were assigned to the primary reaction product $SO_3{}^{2-}$ in the $Tl^+{}_2SO_3{}^{2-}$ triple ion, with an indicated symmetry of lower than C_{3v} due to ion pairing. The ν_3 antisymmetric stretching mode was shifted to higher frequencies, relative to the crystalline solid, and split by 20 cm^{-1}, in a manner similar to that for the isoelectronic $ClO_3{}^-$ anion. A second set of absorptions was observed at higher reactant concentrations, in the S–O stretching and bending regions. These bands have been assigned to the $S_2O_5{}^{2-}$ anion in a symmetrical, oxygen-bridged form, in contrast to the asymmetric S–S-linked form observed at room temperature. A band at 776 cm^{-1}, with a single ^{18}O counterpart at 751 cm^{-1}, has been assigned to the antisymmetric stretching mode of the bridging oxygen, in agreement with a number of related, oxygen-bridged species.

Introduction

The salt/molecule reaction technique has been used extensively since its inception 10 years ago in conjunction with matrix isolation for the study of ions in matrices.[1] In this technique, an alkali-metal halide salt molecule is vaporized and codeposited with a Lewis acid, leading to halide ion transfer and ion-pair formation.[2-5] This technique has proven very valuable in forming halogen-containing anions that are not accessible through normal, room-temperature synthetic techniques.

A variety of oxide salts are used as heterogeneous catalysts, with the implication of reactive oxyanion intermediates.[6,7] In order to gain insight into the mechanism by which oxide salts and oxide surfaces serve to catalyze chemical reactions, the salt/molecule technique was recently extended to oxide salt reactions. The vaporization and codeposition of Tl_2O with samples of CO_2 in argon matrices gave rise to a set of infrared absorptions that were assigned to the carbonate anion $CO_3{}^{2-}$ in the $Tl^+{}_2CO_3{}^{2-}$ triple ion.[8] The spectra obtained were in good agreement with those of the alkali-metal carbonates obtained through the direct vaporization of the salt.[9]

The structure and spectral characterization of sulfur oxyanions have been of continuing interest to chemists for years, but in many cases this information has been difficult to obtain. Unfortunately, salts such as the sulfites and disulfites decompose upon vaporization, so that there is not a direct means for isolating these compounds. Consequently, the oxide salt/molecule technique was applied to form and characterize the intermediate sulfur oxyanions formed through the codeposition of Tl_2O with SO_2 in argon and nitrogen matrices.

Experimental Section

All of the experiments conducted in this investigation were carried out on a conventional matrix isolation system, which has been described previously.[10] Tl_2O (Cerac) was the only oxide salt employed in this study, as all of the alkali-metal salts have been shown to decompose rather than vaporize. On the other hand, Tl_2O is known to vaporize without decomposition and yield primarily the monomeric species, with some dimerization.[11] SO_2 (Matheson) and $S^{18}O_2$ (Stohler, 99%, and Cambridge Isotope, 65%) were purified by at least one freeze–thaw cycle under vacuum prior to sample preparation. It was noted that the 99% enriched $S^{18}O_2$ slowly decreased in enrichment over the period of 6–10 months, down to a level of about 80%. Argon and nitrogen, the matrix gases employed for the majority of the experiments, were used without further purification. SO_2 was used as the matrix material in one experiment.

Matrices were deposited at a flow rate of approximately 2 mmol/h for 20–24 h onto a CsI cold window held in the temperature range 12–17 K (the significance of the temperature variation is discussed in a later section). All infrared spectra, both survey and high resolution, were recorded on either a Beckman IR 12 or a Perkin-Elmer 983 infrared spectrophotometer. Some samples were annealed to between 35 and 40 K and then recooled and additional spectra recorded.

Results

Blank experiments of the reactants in this study have been recorded in past research projects[8,12] from this laboratory; additional blank experiments were conducted when needed. All of the blank experiments were in good agreement with literature spectra.[11,28]

$Tl_2O + SO_2$. Tl_2O was vaporized over a range of oven temperatures, from roughly 430 to 500 °C, and codeposited with samples of Ar/SO_2 with dilution ratios from 100/1 to 1000/1. The oven temperature was selected according to the Tl_2O level desired in the particular experiment. However, it was noted that the change in oven temperature had a noticeable effect on the temperature of the cold window, as did the ambient temperature of the cooling water used to keep the vacuum vessel as close to room temperature as possible when the oven was in use. The net effect was a variation in the temperature of the cold window of roughly 5 K, from 12 to 17 K, and this variation played a role in the reaction products formed.

Approximately 35 experiments were performed over a 1-year time, resulting in two distinct sets of product bands. When Tl_2O was vaporized at 430 °C, the cold window remained at 12 K, and the Tl_2O was codeposited with a sample of Ar/SO_2 = 500; product bands were observed at 1086, 1061–1067, 958–974, 558, 548, and 442 cm^{-1}, as can be seen in Figure 1. These bands were generally noted when the cold window temperature was near 12 K, and the M/R ratio of the SO_2 sample was quite high (500 or 1000/1). A second set of product bands became apparent when the cold window was at a somewhat higher temperature, usually as a consequence

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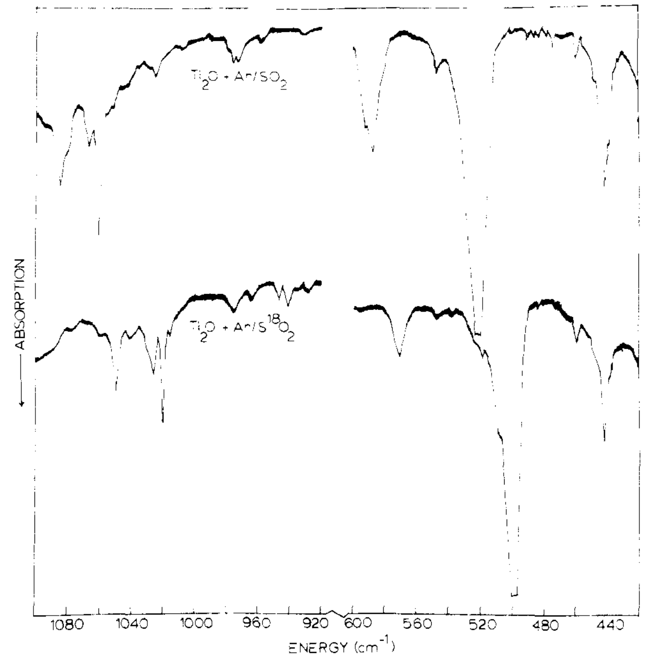

Figure 1. Infrared spectra of the argon matrix reaction products of Tl_2O with SO_2, at high dilutions and at low (12 K) window temperatures. The experiment depicted in the top trace employed normal isotopic SO_2, while 95% ^{18}O-labeled SO_2 was used to obtain the lower trace. The intense band at 520 cm^{-1} in the top trace and at 500 cm^{-1} in the lower trace is due to the bending mode of parent SO_2.

of higher oven temperature, or when high SO_2 concentrations were employed. This second set of bands was located at 1102, 1089, 1050, 1040, 956–973, 882, 776, 657, 608, 595, 495, and 435 cm^{-1}, as shown in Figure 2. While there was considerable similarity of these two band systems, careful comparison of the many spectra obtained allowed a distinction to be made. In one experiment, the sample was annealed to approximately 38 K and recooled to approximately 14 K and further spectra were recorded. A growth was noted in the second set of product bands, while any indication of the first set of product bands disappeared. In some experiments at intermediate concentrations and window temperatures, both sets of bands were observed, as is shown in Figure 3.

Tl_2O was codeposited in a series of experiments with SO_2 in nitrogen matrices, with dilutions ranging from 100/1 to 1000/1. In general, lower yields and less well-defined bands were noted in these N_2 matrix experiments. In addition, only one set of product bands was observed in these experiments, at 1088, 1062, 1057, 1051, 1041, 967, 955, 880, 797, 783, 624, 477, and 435 cm^{-1}; with slight shifts, this set correlates with the second set of bands observed in the argon matrix experiments. Finally, Tl_2O was deposited into a matrix of pure SO_2 in one experiment and a number of moderately intense product bands were noted, at 1074–1034, 940, 871, 638–590, and 430 cm^{-1}. These bands were quite broad and were not well-defined, making accurate determination of band positions and intensities difficult.

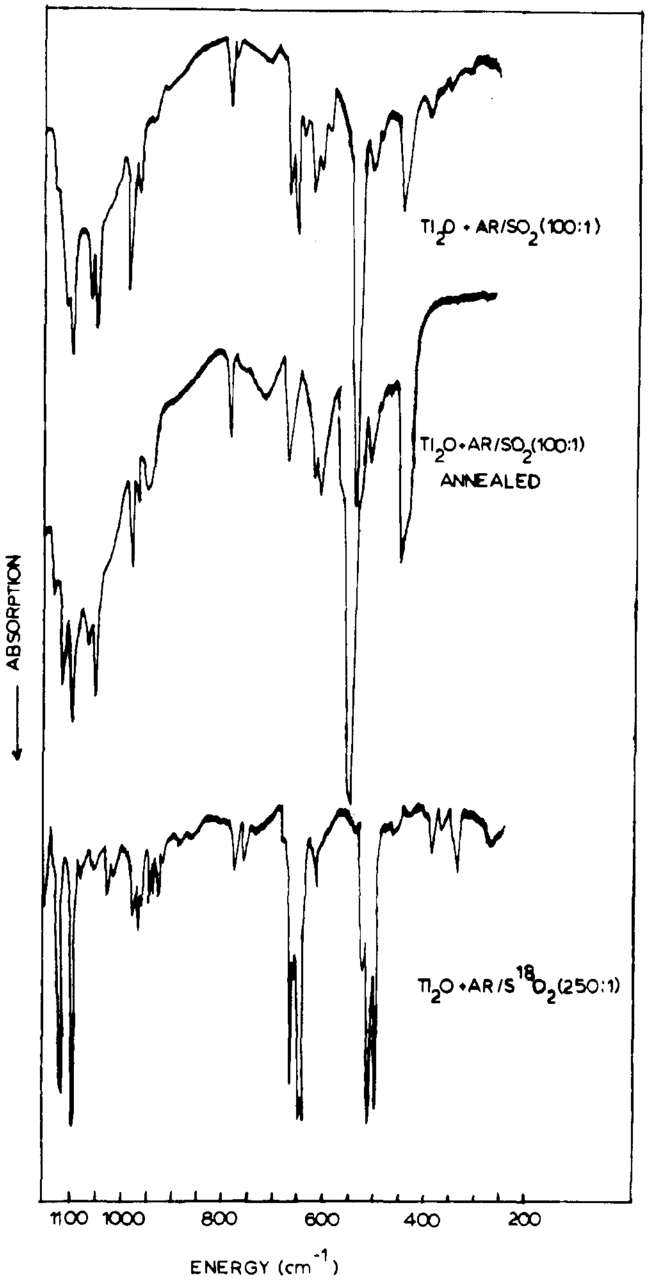

Figure 2. Infrared spectra of the argon matrix reaction products of Tl_2O with SO_2 at high concentration, compared with the spectrum (middle) obtained when the sample was annealed to 38 K and recooled. The bottom trace shows a comparable (slightly more dilute) experiment employing partially ^{18}O-labeled SO_2. Bands present between 300 and 400 cm^{-1} in the bottom trace are also present in blank experiments of Tl_2O in argon and have been assigned previously to Tl_2O aggregates.[11]

$Tl_2O + S^{18}O_2$. Thallium oxide was vaporized and codeposited with isotopically labeled SO_2 in several experiments, with different degrees of isotopic enrichment as well as different cold window temperatures. In the first experiment, with a dilution of $Ar/SO_2 = 500/1$, and 95% ^{18}O enrichment, a single set of bands was observed at 1049, 1020–1026, 941–946, 572, 547, and 442 cm^{-1}. From the location, relative intensities, and experimental conditions it is apparent that this set of bands corresponds to the first set of bands described above when unlabeled SO_2 was employed. In subsequent experiments, dilutions of 250/1 and 100/1 were employed, along with higher oven (and consequently cold window) temperatures, and a second set of bands was observed. These were located at 1088, 1052–1059, 1018–1024, 926–944, 751, 655, and 384 cm^{-1} and correlated with the second set of bands reported above. Since the enrichments in these experiments ranged from 65 to 95 atom % ^{18}O, many of the bands reported above for the pure ^{16}O product species were observed as well.

Discussion

The matrix reaction of Tl_2O in either argon or nitrogen matrices produced a number of product bands which indicated that a reaction had occurred. Moreover, the concentration and temperature dependence of the product bands indicated clearly that more than one species was formed. The product absorptions could be broken down into two distinct sets, the first of which consisted of bands at 1086, 1061–1067, 958–974,

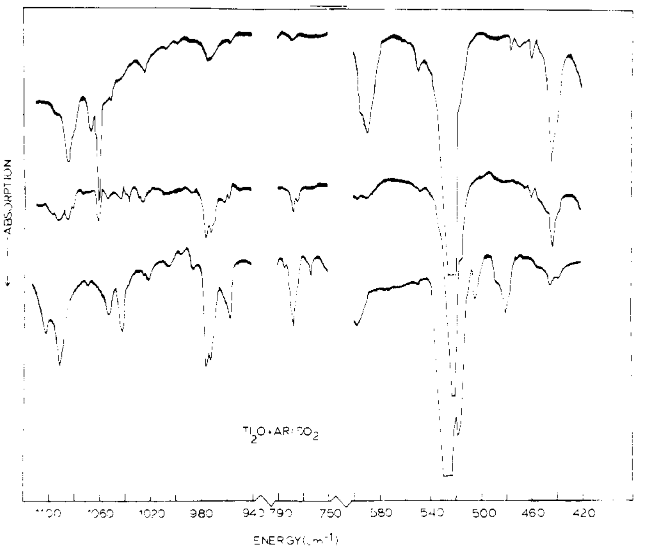

Figure 3. Infrared spectra of the reaction products of Tl_2O with SO_2 over a range of concentrations and conditions. The top trace shows high-dilution, low-temperature conditions (same as the upper trace in Figure 1), while intermediate conditions were employed to obtain the middle trace and high concentrations were employed to obtain the lowest trace.

588, 548, and 442 cm^{-1}. These bands were generally well-defined, as shown in Figure 1, but not particularly persistent. As the SO_2 concentration was increased or the temperature of the cold window increased by a few degrees, these bands diminished in intensity and a second set of bands became prominent. This second set of bands consisted of absorptions at 1102, 1089, 1050, 1040, 958–973, 882, 776, 657, 608, 595, 495, and 435 cm^{-1} and was quite persistent. At high SO_2 concentrations and high (17 K) window temperatures this was the only set of absorptions that could be identified (although the two sets of absorptions were, for the most part, quite close to one another). In addition, when an experiment was conducted in which both sets of bands were observed, and this sample was then annealed to approximately 35 K and recooled, evidence of the first set of absorptions diminished, while the second set of bands persisted and grew. This concentration and diffusion dependence marks the second set of bands as due to larger aggregate species, while the first set of bands, which dominated at high dilution, is likely due to the 1:1 reaction product of Tl_2O with SO_2.

Identification of $SO_3{}^{2-}$. Previous studies with the salt/molecule technique and halide salts have resulted in halide anion transfer to form a product anion in an ion pair. Initial studies[8] of the oxide salt/molecule technique yielded similar results, i.e., that formation of an oxyanion occurred in a triple ion with two Tl^+ cations. In view of these results, formation of the $SO_3{}^{2-}$ anion in the $Tl^+{}_2SO_3{}^{2-}$ triple ion is anticipated for the 1:1 reaction product. The sulfite anion, $SO_3{}^{2-}$, is well-known and its vibrational spectrum well-established.[13] In crystals and in solution the anion has C_{3v} symmetry, with 2 A_1 and 2 E normal vibrational modes. The symmetric stretching and bending modes have been identified near 961 and 633 cm^{-1} (ν_1 and ν_2), while the degenerate antisymmetric stretching and bending modes (ν_3 and ν_4) have been located near 1010 and 496 cm^{-1}, although some variation with cation has been noted. The symmetry of the sulfite anion in the isolated triple ion will, in all likelihood, be lower than C_{3v}, and a splitting of ν_3 and ν_4 is expected. Thus, one anticipates six distinct infrared absorptions for the isolated $Tl_2{}^+SO_3{}^{2-}$ triple ion, in the proximity of the frequencies indicated above. Devlin et al.[14a] observed quite similar results for the isoelectronic $ClO_3{}^-$ anion in $M^+ClO_3{}^-$ ion pairs, namely a cation-dependent splitting of the two degenerate modes and slight shifts of the symmetric modes. Beattie and Parkinson,[14b] on the other hand, have recently suggested that the $MClO_3$ ion pairs maintain C_{3v} symmetry, without a splitting of ν_3. While the present work does not shed any additional light on this dispute, it is likely that in the $Tl^+{}_2SO_3{}^{2-}$ *triple* ion the symmetry is less than C_{3v}.

Examination of the top trace of Figure 1 suggests a correlation of the first set of product bands with the internal vibrational modes of the $SO_3{}^{2-}$ anion in the $Tl^+{}_2SO_3{}^{2-}$ triple ion. The two absorptions near 1064 and 1086 cm^{-1} are assigned to the two components of ν_3, split by cation distortion and shifted to higher energy. However, the presence of *two* cations in the $Tl^+{}_2SO_3{}^{2-}$ triple ion, if symmetrically located, may actually minimize the perturbation to the sulfite anion. Gingerich[15] observed splittings of roughly 30 cm^{-1} for the $M^+{}_2SO_4{}^{2-}$ triple ions, which are comparable to the values obtained here. The shift of ν_3 to higher energy relative to that of crystalline Na_2SO_3 is of interest as well (no infrared spectrum of crystalline Tl_2SO_3 could be found in the literature). One explanation follows from Devlin's observation that for $Tl^+NO_3{}^-$ the covalent contribution to anion distortion was the same order of magnitude as that from cation polarization of the anion.[16] Consequently, one might invoke some covalent interaction from the Tl^+ cations, which is consistent with the much higher ionization potential of thallium (6.31 eV) compared to those of the alkali metals (5.14 eV for Na to 3.89 eV for Cs).[17] This higher ionization potential (or larger covalent interaction) would withdraw some electron density from the $SO_3{}^{2-}$ anion, increase slightly the S–O stretching force constant, and cause a shift to higher energy.

An alternative explanation for this shift to higher energy arises from the observation of Cotton et al. that, in dimethyl sulfoxide complexes, coordination through the sulfur to a positive center raised the S–O force constant compared to coordination through the oxygens.[18] Consequently, if the thallium cations coordinate to the sulfur in the $Tl^+{}_2SO_3{}^{2-}$ triple ion, one would anticipate a shift to higher energies. This latter explanation requires the assumption of interaction between the sulfur atom and the thallium cations, while the former explanation, invoking a covalent contribution from the thallium, does not require this assumption. On this basis, the former explanation is preferred slightly, but the spectra do not provide a basis for explicit differentiation between these models.

Assignment of the remaining bands to the vibrational modes of the $SO_3{}^{2-}$ anion is relatively straightforward, by comparison to the spectrum of the crystalline anion. The doublet centered near 966 cm^{-1} is assigned to the symmetric stretching vibration, probably split by slightly differing locations of the cations in the triple ion; it might be noted that Devlin observed a similar splitting of ν_1 in the $M^+ClO_3{}^-$ ion pair. The single band at 588 cm^{-1} is assigned to the symmetric deformation mode, shifted down somewhat from its position in the crystalline solid. Finally, the shoulder at 548 cm^{-1} and the band at 442 cm^{-1} are assigned to the two components of the antisymmetric deformation mode, which lies at 496 cm^{-1} in the C_{3v} anion. Interestingly, the splitting of the two components about the unperturbed position is centrosymmetric, as contrasted to the ν_3 mode. Table I lists band positions and assignments for the $Tl_2{}^+SO_3{}^{2-}$ triple ion and related species.

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Table I. Frequencies and Band Assignments for the SO_3^{2-} Anion and Related Species[c]

species	ν_1	ν_2	ν_{3A}	ν_{3B}	ν_{4A}	ν_{4B}	ref
$Tl^+{}_2SO_3^{2-}$	958, 974	588	1061, 1067	1086	442	548	*a*
$Tl^+{}_2S^{16}O^{18}O_2^{2-}$	941, 946	572	1020, 1026	1049	442	547	*a*
SO_3^{2-} (cryst)[b]	961	633	1010		496		13
$K^+ClO_3^-$ (matrix)	917, 927	625	968	1017	479	508	14a

[a] Matrix spectra, this work. [b] Na^+ cation. [c] Band positions in cm^{-1}.

Identification of $S_2O_5^{2-}$. The second set of bands observed in these experiments showed growth upon an increase in SO_2 concentration, higher cold window temperature, or annealing of the matrix. These points suggest an aggregate species, involving more than one of either or both of the reactants. Chemically, the most likely species is the disulfite anion $S_2O_5^{2-}$ in the $Tl^+{}_2S_2O_5^{2-}$ triple ion. This anion is relatively well-known,[19,20] although considerable question remains as to its structure (see below). Other possible aggregate species include the 1:3 reaction product $S_3O_7^{2-}$, but this would not seem likely without the prior formation of the 1:2 reaction product, $S_2O_5^{2-}$. Since only one aggregate species was observed, the $S_3O_7^{2-}$ species is not the best candidate. Another alternative is the 2:1 reaction product, namely the SO_4^{4-} species in the $Tl^+{}_4SO_4^{4-}$ complex. One would expect very limited stability of such an anion, and if at all stable, it would likely absorb at considerably lower energies than the SO_3^{2-} anion. On the other hand, the disulfite anion $S_2O_5^{2-}$ is chemically quite similar to the SO_3^{2-} anion and should absorb in a similar spectral region, as is observed. All of these arguments indicate that the second set of bands observed in this study is best assigned to the $S_2O_5^{2-}$ anion in the $Tl^+{}_2S_2O_5^{2-}$ triple ion.

While the disulfite anion has been identified in a number of crystals, the determination of the structure has been inconsistent. Simon and co-workers[21] proposed the symmetrical oxygen-bridged structure $O_2SOSO_2^{2-}$ on the basis of Raman data, while a number of groups[22-24] subsequently disputed this conclusion, preferring an unsymmetrical, C_s structure with an S–S linkage. In all of these vibrational studies the spectra obtained were nearly identical, but spectral interpretation differed. The only X-ray diffraction determination of the structure also led to the unsymmetrical $O_3SSO_2^{2-}$ form.[25] The spectra obtained here are, for the most part, similar to those obtained by previous workers (given the very different environments under consideration), with two significant exceptions as can be seen in Table II. First, no bands were observed below 435 cm^{-1}, while the previous workers[19,23] observed a band near 235 cm^{-1}. This band has been assigned to the S–S stretching mode of the unsymmetrical form, and its absence here suggests that under matrix isolation conditions the unsymmetrical form is not present. More importantly, a sharp, well-defined band was observed in the present work at 776 cm^{-1}, which was not observed by any of the previous workers. This band lies quite close to the antisymmetric stretching mode of the bridging oxygen in a number of complex anions that are known to contain an oxygen bridge.[26,27] This mode occurs at 805 cm^{-1} for $S_2O_7^{2-}$, at 770 cm^{-1} for $V_2O_7^{4-}$ (in the thallium salt), and at 760 cm^{-1} for the neutral $S_2O_5Cl_2$ molecule. In addition, the band at 776 cm^{-1} showed a strong ^{18}O shift, to 751 cm^{-1} when $S^{18}O_2$ was employed with *no* intermediate ^{16}O, ^{18}O counterpart, indicating the vibration of a *single* oxygen atom. The proximity to the antisymmetric stretching frequency of other known oxygen-bridged compounds, the isotopic behavior, and the lack of observation of a S–S stretching mode all suggest that the $S_2O_5^{2-}$ anion is present in the symmetrical $O_2SOSO_2^{2-}$ form under these conditions.

Table II. Vibrational Spectra of the $S_2O_5^{2-}$ Anion and Related Species[c]

$S_2O_5^{2-}$ (matrix)[a]	$S_2O_5^{2-}$ ((80%) ^{18}O, matrix)[a]	$K_2S_2O_5$ (solid)[b]
1102	. . .	. . .
1089	1088	1081
1050	1052, 1059	1058
1040	960, 972	. . .
956, 973	926, 944	973
882	. . .	. . .
776	774	. . .
	751	. . .
657	655	668
595	. . .	649
495	. . .	584
435	. . .	509
		439
		313
		236
		210

[a] This work. [b] Reference 19. [c] Band positions in cm^{-1}.

An additional argument in support of the symmetric form of the $S_2O_5^{2-}$ anion comes from the bands assigned to the terminal S–O vibrations. Only four bands were observed in this region, and they were relatively close together, suggesting two nearly uncoupled SO_2^- terminal groups. On the other hand, if the structure was unsymmetrical, the anion might be viewed as a nearly uncoupled SO_2^- unit and SO_3^- unit. This latter group might then be compared to the XSO_3^- anions, all of which show very intense absorptions near 1200 cm^{-1}, due to the antisymmetric SO_3 stretch. The absence of a band near 1200 cm^{-1} in the current work suggests an SO_3-type unit is not present in the product species and supports the above assignment to an oxygen-bridged species. Whether this represents the most stable form of the anion, or whether this simply indicates that the structure is trapped before equilibration, is not apparent, but previous studies have shown that the room-temperature structure in a variety of crystals is unsymmetrical.

For the symmetric, oxygen-bridging species observed here, there should be two additional vibrational modes. One is the symmetrical stretching motion of the two SO_2 units with respect to the bridging oxygen, and the other is the bending motion of the oxygen bridge. The former vibration should lie within the spectral range of the instrument used here but should be quite weak, and with the yield of product obtained here, this mode probably escaped detection. The second mode should lie at very low energies, which are not accessible with the instrumentation in use.

Mechanistic Considerations. One unusual aspect of the current investigation was the difficulty of formation of the 1:1 product, namely the SO_3^{2-} anion. In the majority of experiments, the predominant product species was the $S_2O_5^{2-}$ anion. Only at very high dilution and low cold window temperatures was the $Tl^+{}_2SO_3^{2-}$ species isolated, and in N_2 matrices it was never observed. This latter observation is consistent with the

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lower freezing point of N_2 relative to argon, and hence a slightly slower rate of freezing during the deposition process and slightly greater mobility of the reactant species. It is also interesting to note that a recent study[24] of the SO_2/H_2O system found the large majority of the sulfur either in the form of SO_2 or as $S_2O_5^{2-}$, while very little of the intermediate SO_3^{2-} was noted.

The disulfite $S_2O_5^{2-}$ anion might form by one of several routes under these conditions. One is the simultaneous, three-body collision of two SO_2 molecules and Tl_2O, but this is quite unlikely at the concentrations employed. More likely, formation of $S_2O_5^{2-}$ involves initial formation of the SO_3^{2-} anion, followed by addition of a second SO_2 unit to form the final product anion. The fact that the ^{18}O label appears in the bridging position as well as in the terminal oxygen positions is consistent with this view as well. If this is the mechanism by which $S_2O_5^{2-}$ is formed, then the addition of SO_2 to SO_3^{2-} must be very facile, with effectively no activation energy, since in many cases nearly all of the SO_3^{2-} is converted to $S_2O_5^{2-}$ during the condensation process. A final possible mechanism, the reaction of Tl_2O with sulfur dioxide dimer, $(SO_2)_2$, cannot be ruled out but does not seem likely in that this dimer is weakly bound and should not be abundant at the concentrations employed.

Conclusions

The reaction of thallium(I) oxide, Tl_2O, with SO_2 under matrix isolation conditions has given rise to two distinct product species, the SO_3^{2-} and $S_2O_5^{2-}$ anions, each in a triple ion with two Tl^+ cations. The infrared spectrum of the $Tl^+{}_2SO_3^{2-}$ species showed a lowering of the SO_3^{2-} symmetry due to ion pairing, in a manner similar to that for the $M^+ClO_3^-$ ion pairs. The infrared spectrum of $S_2O_5^{2-}$ indicated an oxygen-bridged structure under these conditions, rather than the unsymmetrical S–S linkage found for the room-temperature, crystalline material. Finally, further evidence has been obtained to support the utility of the oxide salt/molecule technique in forming and isolating oxygen-containing anions that either decompose upon vaporization or are not stable under room-temperature conditions.

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Registry No. Tl_2O, 1314-12-1; SO_2, 7446-09-5; Tl_2SO_3, 13453-46-8; $S_2O_5^{2-}$, 23134-05-6; ^{18}O, 14797-71-8.

Contribution from the Corporate Research Science Laboratories,
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EXAFS Studies of Amorphous Molybdenum and Tungsten Trisulfides and Triselenides

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The structure of the amorphous molybdenum and tungsten trisulfides and triselenides has been investigated by using X-ray absorption spectroscopy. Analysis of the metal EXAFS data revealed metal–metal distances between 2.74 and 2.79 Å, as well as normal, but disordered, metal–chalcogen distances (Mo–S = 2.44 Å, W–S = 2.41 Å, Mo–Se = 2.53 Å, W–Se = 2.55 Å). The selenium EXAFS of the triselenides shows Se–Se distances of 2.35–2.37 Å. It is proposed that the important structural unit of these amorphous materials is a binuclear metal site with a triple bridge consisting of one chalcide ion and one dichalcide ion. Several results of general applicability for EXAFS analysis were obtained during the course of this work. Procedures using experimental amplitude functions have been developed that yield meaningful estimates of static disorder. The utility of curve-fitting procedures for L_{III} edge EXAFS analysis has also been demonstrated, and screening effects on second-shell EXAFS amplitudes have been quantified.

Introduction

The amorphous trichalcides MoS_3, WS_3, $MoSe_3$, and WSe_3 have interesting electrochemical and physical properties.[1] They are normally prepared by thermal decomposition of the corresponding diammonium tetrachalcidometalate salts,[2] although similar materials can be made by solution procedures.[3] X-ray diffraction analysis shows that the trichalcides prepared by either method are amorphous in nature,[4–6] a property that has hindered their characterization on an atomic scale. Stimulated in part by the fact that MoS_3 can be used as a cathode material to construct a high-energy-density alkali-metal battery,[1] the structural characterization of these materials by a variety of methods has been undertaken.[6,7] In this paper, the outcome of an X-ray absorption study of these materials is reported. The EXAFS (extended X-ray absorption fine structure) data, interpreted by comparison with the corresponding crystalline $(NH_4)_2MX_4$ and MX_2 compounds, clearly demonstrate metal–metal bonding in all of the MX_3 materials examined, with metal–metal bond lengths shorter than those previously suggested by X-ray radial distribution function analysis.[5]

Several advances in the experimental approach to the analysis of EXAFS data were achieved in the course of this work. First, it is shown that reliable Debye–Waller factors can be obtained by the combination of vibrational normal-mode calculations and curve-fitting techniques and that these factors are useful for interpreting the EXAFS of amorphous materials. It has also been shown that these techniques are applicable to L_{III} edges as well as K edges. Finally, there has

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