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Infrared Matrix-Isolation Investigation of the Mono- and Dithiocarbonate Anions

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The oxide-transfer technique, involving O^{2-} transfer from Tl_2O to a suitable acceptor, has been coupled with matrix isolation for the synthesis and infrared spectroscopic characterization of the mono- and dithiocarbonate anions, CO_2S^{2-} and COS_2^{2-}, each in a triple ion with two Tl^+ cations. CO_2^{2-} was characterized by sharp, intense carbon–oxygen stretching vibrations at 1445 and 1202 cm^{-1} and a carbon–sulfur stretching mode at 603 cm^{-1}. These assignments were confirmed by ^{13}C and ^{18}O isotopic substitution and by normal-coordinate calculations. The two most intense bands of the COS_2^{2-} anion, the C–O stretch and the antisymmetric C–S stretch, were identified at 1506 and 606 cm^{-1}, respectively, and were fit to an approximate force field. The calculated force constants suggest increased localization of the π bonding on the carbon–oxygen bond(s) as the number of sulfur atoms in the anion is increased.

Introduction

The substitution of sulfur for oxygen in a number of species, both ions and neutrals, alters signficantly the bonding and subsequent physical properties of these species.[1] For relatively large systems, quantification of these changes is difficult; by comparison, small inorganic systems that lend themselves to normal-coordinate calculations may provide some insight in this area. The carbonate/thiocarbonate ion system is one that may be potentially informative in this respect, by examining the force field for the carbonate anion and the mono-, di-, and trisubstituted thiocarbonates. While the carbonate anion is well-known and characterized,[2,3] and some data are available for the CS_3^{2-} anion,[4] very little is known about the intermediate species CO_2S^{2-} and COS_2^{2-}, which likely disproportionate in solution to CO_3^{2-} and CS_3^{2-}. Early workers in the textile field suggested the existence of the COS_2^{2-} anion as an intermediate in the reaction of NaOH with CS_2, but no material was isolated and a disproportionation reaction was postulated.[5] Certainly, no vibrational spectra or force fields are available for these intermediate species. Two theoretical studies[6] have investigated this system at different levels of calculation; the first employed[6a] an LCAO approach and found a systematic shift in the lowest π to π^* transition upon increasing sulfur atom substitution. The second, at the STO-6G level, found that the C–O and C–S distances decreased upon substitution, while the net charge on the carbon underwent a change in polarity from positive to negative as sulfur atom substitution increased.[6b]

The salt/molecule technique was developed for use in conjunction with matrix isolation for the study of anionic species ion paired in inert matrices.[7] The initial studies employing this technique were concerned with halide transfer from an alkali halide to a Lewis acid, leading to anion formation.[8-10] Recently, this technique was extended to oxide-transfer reactions, and the carbonate anion CO_3^{2-} was isolated and characterized in the isolated $Tl^+{}_2CO_3^{2-}$ triple ion.[11] The spectra obtained in this fashion were nearly identical with those obtained through the direct vaporization of alkali-metal carbonates into nitrogen matrices.[12] The application of oxide-transfer reactions from Tl_2O to OCS and CS_2 provides a novel means for the formation and isolation of the intermediate thiocarbonate anions, from which infrared spectra and a force field may be determined. This information, in turn, can be used to investigate the differences arising from the substitution of sulfur for oxygen in small inorganic systems.

Experimental Section

All of the experiments conducted in this investigation were carried out on a conventional matrix-isolation system that has been described previously.[13] Tl_2O (Cerac) was the only oxide salt employed in this study, as all of the alkali oxide salts have been shown to decompose prior to vaporization. On the other hand, Tl_2O is known to vaporize without decomposition[14] and yield primarily the monomeric species, with some dimerization. In addition, a few experiments were carried out employing Tl_2S; little is known about the vaporization kinetics of Tl_2S, and some indication of decomposition was noted. OCS (Matheson) and CS_2 (Fisher) were purified by at least one freeze–thaw cycle under vacuum prior to sample preparation. $O^{13}CS$ and ^{18}OCS were synthesized by the reaction of the appropriate labeled CO (^{13}CO and $C^{18}O$, Merck, 99%) with elemental sulfur at 350 °C for approximately 24 h in a stainless-steel vessel. While incomplete conversion of CO to OCS was obtained, sufficient product was separated and purified for the necessary experiments. Argon was used as the matrix gas in all experiments and was used without further purification.

Matrices were deposited at a flow rate of approximately 2 mmol/h for 20–24 h onto a cold window held near 12 K. All infrared spectra, both survey and high resolution, were recorded on a Perkin-Elmer 983 infrared spectrometer with computer data handling capabilities. Some samples were annealed to between 35 and 40 K and then recooled to 12 K for additional spectra.

Results

Prior to investigation of the reaction products of Tl_2O with OCS, CS_2, and isotopically labeled species, blank experiments were conducted on each of the reactants alone, at one or more concentrations. In each case, the observed spectra were in good agreement with gas-phase spectra, and matrix spectra where available.[15,16] Blank experiments on $O^{13}CS$ and ^{18}OCS indicated a level of isotopic enrichment comparable to that indicated by the manufacturer for the carbon monoxide precursor. Blank experiments of Tl_2S repeatedly showed relatively intense bands due to SO_2 and CO_2, along with a band of moderate intensity at 475 cm^{-1} that is tentatively assigned to matrix-isolated Tl_2S.

Tl_2O + OCS. Tl_2O was vaporized and codeposited with carbonyl sulfide in a number of experiments, with dilution ratios in argon of between 100/1 and 1000/1 (Ar/OCS). When Tl_2O was codeposited with a sample of Ar/OCS = 1000, three new , sharp infrared absorptions were noted, which could not be assigned to either parent species. These product bands were located at 603, 1202, and 1445 cm^{-1} and were quite well-defined, as shown in Figure 1. When the concentration of OCS in argon was increased stepwise from 500/1 to 200/1 and finally to 100/1 and codeposited with a comparable level of Tl_2O, all three product bands were observed to grow, and at the same rate. Consequently, the relative

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(1) Oae, S. "The Organic Chemistry of Sulfur"; Plenum Press: New York, 1977.

(2) Bates, J. B.; Brooker, M. J.; Quist, A. S.; Boyd, G. E. *J. Phys. Chem.* **1972**, *76*, 1565.

(3) Bhagavantum, S.; Venkatarayudu, T. *Proc.—Ind. Acad. Sci., Sect. A* **1939**, *9A*, 224.

(4) Muller, A.; Mohan, N.; Cristophliemk, P.; Tossidis, I.; Drager, M. *Spectrochim. Acta, Part A* **1973**, *29A*, 1345.

(5) (a) Weeldenburg, J. G. *Recl. Trav. Chim. Pays. Bas* **1928**, *47*, 496. (b) Herrent, P.; Jnoff, G. *J. Polym. Sci.* **1948**, *3*, 487. (c) Herrent, P.; Jnoff, G. *J. Polym. Sci.* **1950**, *5*, 727. (d) Hoevenkamp, S. G. *J. Polym. Sci., Part C* **1963**, *2*, 341. (e) Drager, M.; Gattow, G. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 868.

(6) (a) Ozias, Y.; Reynard, L. *Theor. Chim. Acta* **1971**, *20*, 51. (b) Ozias, Y.; Julg, A. *J. Mol. Struct.* **1979**, *57*, 183.

(7) Ault, B. S. *ACS Symp. Ser.* **1982**, No. 179.

(8) Ault, B. S.; Andrews, L. *J. Am. Chem. Soc.* **1975**, *97*, 3824.

(9) Ault, B. S. *J. Phys. Chem.* **1979**, *83*, 837.

(10) Garger, K.; Ault, B. S. *Inorg. Chem.* **1983**, *22*, 2509.

(11) David, S. J.; Ault, B. S. *J. Phys. Chem.* **1982**, *86*, 4618.

(12) Ogden, J. S.; Williams, S. J. *J. Chem. Soc. Dalton Trans.* **1981**, 456.

(13) Ault, B. S. *J. Am. Chem. Soc.* **1978**, *100*, 2426.

(14) Brom, J. M.; Devore, T.; Franzen, H. F. *J. Chem. Phys.* **1971**, *54*, 2742.

(15) Jeannotte, A. C.; Overend, J. *Spectrochim. Acta, Part A* **1979**, *35A*, 1213.

(16) Wentink, T. *J. Chem. Phys.* **1958**, *29*, 188.

0020-1669/85/1324-1048$01.50/0

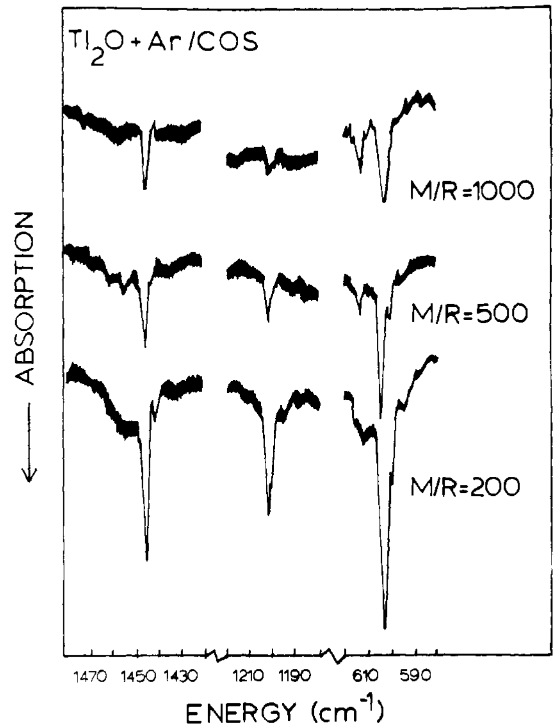

Figure 1. Infrared spectra of the products arising from the codeposition of Tl_2O with OCS into argon matrices, at dilutions of 1000/1, 500/1 and 200/1, over selected regions.

intensities of these three product bands remained constant over a range of experiments. When the oven temperature, and hence rate of vaporization of Tl_2O, was increased, the three product bands again grew and continued to maintain their relative intensities. However, even at these higher concentration levels, no additional product bands were observed in the spectrum. Infrared spectra of the reaction products of Tl_2O with OCS at several different concentration ratios (M/R) are shown in Figure 1.

Tl_2O + $O^{13}CS$. This pair of reactants was investigated in a single experiment at a concentration of Ar/$O^{13}CS$ = 500 and an enrichment of 95% ^{13}C. Three product bands were observed in the final spectrum that could not be attributed to parent species, just as in experiments employing the normal carbon isotope. These bands appeared at 602, 1173, and 1408 cm^{-1}, all shifted down in energy from the bands observed with normal isotopic OCS. Nonetheless, these three bands showed the same relative intensities as reported above, as can be seen in Figure 2.

Tl_2O + ^{18}OCS. Tl_2O was vaporized and codeposited in two experiments with samples of ^{18}OCS in argon, at concentrations of 500/1 and 250/1. In each experiment, three new product bands were detected, analogous to those reported above. These three bands were located at 603, 1198, and 1422 cm^{-1} and showed the same relative intensities as the product bands observed with the normal isotopes of OCS, as can be seen in Figure 2.

$Tl_2{}^{16}O/Tl_2{}^{18}O$ + OCS. A mixture of ^{16}O and ^{18}O Tl_2O, with approximately a 35% ^{18}O enrichment was vaporized and codeposited with normal isotopic OCS at a concentration of 500/1 in argon. Five product bands were noted in this experiment at 603, 1198, 1202, 1422, and 1445 cm^{-1}; the pairs at 1198/1202 and 1422/1445 cm^{-1} showed an intensity ratio of about $^1/_2$, which matched the level of isotopic enrichment. The bands at 603, 1202, and 1445 cm^{-1} matched those observed in the reaction of $Tl_2{}^{16}O$ with OCS, while the bands at 603, 1198, and 1422 cm^{-1} matched those observed when $Tl_2{}^{16}O$ was codeposited with ^{18}OCS. Finally, it is noteworthy that the band at 603 cm^{-1} in this experiment was relatively more intense compared to the upper bands than in experiments employing normal isotopes of each reactant.

Tl_2O + CS_2. These two reactants were codeposited in a number of experiments, with M/R values ranging from 200/1 to 2000/1. When Tl_2O was codeposited with a sample of Ar/CS_2 = 2000, two distinct new product bands were observed in the final spectrum, which could not be attributed to either parent species. These new bands were very sharp, were quite intense, and were located at 606 and 1506 cm^{-1}. This latter band was on the low-energy side of the antisymmetric stretching band of unreacted parent CS_2 but at low concentrations was quite distinct and separate. When the Ar/CS_2 concentrations were increased to 500, 200, and 100, the same two bands were detected, and with a constant ratio of intensities. No additional bands were noted in the spectrum, and the region between 800 and 1100 cm^{-1} was clear and devoid of any absorptions. These two product bands are shown in Figure 3.

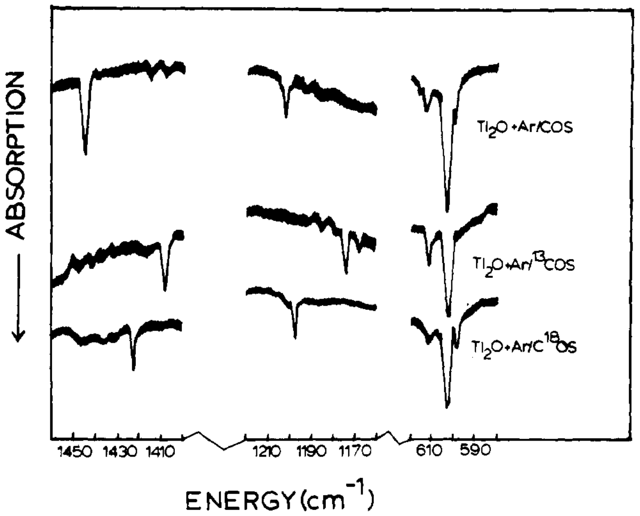

Figure 2. Infrared spectra of the reaction products from the codeposition of Tl_2O with normal isotopic OCS (top trace), with $O^{13}CS$ (middle trace), and with ^{18}OCS (bottom trace), all at M/R = 500.

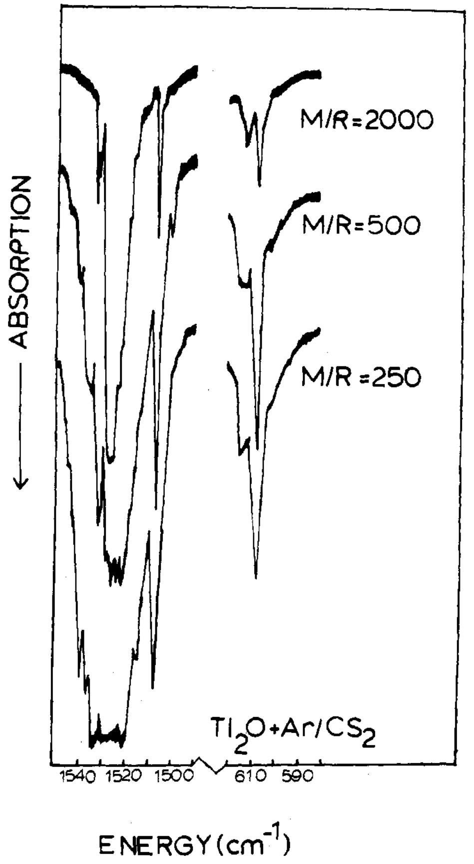

Figure 3. Infrared spectra of the products arising from the codeposition of Tl_2O with samples of Ar/CS_2 at M/R values of 2000, 500, and 250 cm^{-1}, over selected spectral regions.

$Tl_2{}^{16}O/Tl_2{}^{18}O$ + CS_2. When CS_2 was codeposited with a mixture of $Tl_2{}^{16}O/Tl_2{}^{18}O$ containing about 35% enrichment in

^{18}O, three distinct product bands were observed, at 574, 606, and 1506 cm^{-1}. There was some indication of a product band in the region near 1475 cm^{-1}, but this region was partially obscured by the antisymmetric stretching mode of $^{13}CS_2$ in natural abundance, which at a concentration of 500/1 in argon had an absorbance of approximately 0.2 unit.

$Tl_2S + CS_2$. Tl_2S was heated, and the vaporization products were codeposited with samples of Ar/CO_2 in a number of experiments. As noted above, substantial amounts of SO_2 were detected, as well as the band at 475 cm^{-1} that is tentatively assigned to parent Tl_2S. In addition, weak absorptions were noted in each experiment near 600 and 1445 cm^{-1}, matching the two most intense bands observed in the experiment reported above involving Tl_2O and OCS.

Discussion

The codeposition of Tl_2O with OCS into argon matrices gave rise to at least one product species, characterized by three infrared absorptions at 603, 1202, and 1445 cm^{-1}. These were quite intense in the more concentrated experiments, with M/R up to 100, and persisted at dilutions as great as 1000/1. Moreover, these three bands maintained a constant intensity ratio over this wide range of concentrations, marking the three as arising from a single product species. When isotopically labeled OCS was employed (^{13}C or ^{18}O), each of the product bands showed a measurable shift, indicating the incorporation of these labels into the product species. In addition, when $Tl_2{}^{18}O$ was codeposited with OCS, the identical set of product bands to those of the $Tl_2O + {}^{18}OCS$ experiment was obtained, indicating that the same product species is formed through the two different routes. Finally, the codeposition of Tl_2S with CO_2 gave rise to the same set of product bands, although weak, as the reaction of Tl_2O + OCS. All of these data are strongly suggestive of a 1:1 reaction product, and in view of the previous results of the Tl_2O/CO_2 system[11] in which the $CO_3{}^{2-}$ anion was obtained in contact with two Tl^+ cations, these three product absorptions are assigned to the previously unreported monothiocarbonate anion, CO_2S^{2-}, in the $Tl^+{}_2CO_2S^{2-}$ triple ion.

Band assignments for the three product bands are relatively straightforward, by comparison to the earlier results on the $Tl^+{}_2CO_3{}^{2-}$ triple ion, and the known Raman spectrum[4] of Ba^{2+}-$CS_3{}^{2-}$. Two C–O stretching modes are anticipated for this anion, a symmetric and an antisymmetric combination; for the $Tl^+{}_2CO_3{}^{2-}$ triple ion these were located at 1506 and 1311 cm^{-1}. While shifted slightly to lower energy, the bands at 1445 and 1202 cm^{-1} are readily assigned to the two C–O stretching vibrations. Both by analogy to the carbonate study and by relative intensities, the upper band at 1445 cm^{-1} is assigned to the antisymmetric mode and the lower, less intense, band at 1202 cm^{-1} to the symmetric mode. The remaining product band, at 603 cm^{-1}, lies slightly to higher energies of the symmetric C–S stretching mode of the $CS_3{}^{2-}$ anion; upon reduction of symmetry from D_{3h} ($CS_3{}^{2-}$) to C_{2v} (CO_2S^{-2}) the totally symmetric stretching mode in D_{3h} symmetry transforms[17] into the stretching mode of the unique atom, i.e. S, so that the C–S stretching mode of the CO_2S^{2-} anion is anticipated in the vicinity of the symmetric stretching mode of $CS_3{}^{2-}$. In view of this, the band at 603 cm^{-1} is assigned to the C–S stretching mode of the CO_2S^{2-} anion in the $Tl^+{}_2CO_2S^{2-}$ triple ion.

A number of additional vibrational modes are anticipated for this product anion, all of which are bending or angle deformation modes. Those involving substantial sulfur atom motion are anticipated at low energies and should be relatively weak as well. The out-of-plane deformation mode involves considerable oxygen atom motion and should lie above 700 cm^{-1} (845 cm^{-1} for $CO_3{}^{2-}$). However, this mode was extremely weak for the $Tl^+{}_2CO_3{}^{2-}$ triple ion and was observed only in the highest yield experiments. Even in the best experiments conducted here, the yield of the CO_2S^{2-} anion, as judged by band intensities, never came close to the yield of the $CO_3{}^{2-}$ anion. Hence, lack of observation of this mode due to lack of intensity is not surprising. The remaining bending mode is the in-plane O–C–O angle bend, which correlates to one component of the in-plane bending mode of the $CO_3{}^{2-}$ anion near 700 cm^{-1}. Using relative intensities of the antisymmetric C–O stretching modes of the $CO_3{}^{2-}$ anion (1506 cm^{-1}) and the CO_2S^{2-} anion (1445 cm^{-1}) as a guide, one would predict that this mode should be weak but potentially observable for the CO_2S^{2-} anion. Again, by analogy to the carbonate anion, this mode should lie near or slightly below 700 cm^{-1}. Parent Tl_2O absorbs strongly from roughly 650 to 630 cm^{-1} and may obscure this product absorption, which is anticipated to be relatively weak. In any event, no bands were noted in any experiment that could be assigned to this deformation mode.

The codeposition of Tl_2O with CS_2 into argon matrices gave rise to two product bands, at 606 and 1506 cm^{-1}. While the upper band was just to the low-energy side of parent CS_2, both were sharp, distinct bands that maintain a constant intensity ratio throughout a range of experiment. This marks these two absorptions as arising from a single absorber, and in view of past results of the oxide salt reaction technique and the above results for the CO_2S^{2-} system, these two bands are assigned to the dithiocarbonate anion, $COS_2{}^{2-}$, in the $Tl^+{}_2COS_2{}^{2-}$ triple ion. One C–O stretching mode is anticipated for this species, and certainly the band at 1506 cm^{-1} is a logical candidate for such an assignment. When $Tl_2{}^{18}O$ was employed, a new product band was tentatively identified near 1475 cm^{-1} but was partially masked by the absorption of $^{13}CS_2$ in natural abundance. While this observation is somewhat tentative, the location is certainly appropriate for an ^{18}O counterpart of the 1506-cm^{-1} band.

The $COS_2{}^{2-}$ anion should have two C–S stretching modes, a symmetric and an antisymmetric combination. Only one product band, at 606 cm^{-1}, was observed that can be assigned to one of these modes. Which is the better assignment and why the second mode was not observed are questions that are not readily answered from the spectra alone. As described below, simple normal-coordinate calculations were carried out and support assignment of the 606-cm^{-1} absorption to the antisymmetric C–S stretching mode. If this assignment is correct, the symmetric C–S stretching mode is calculated to lie near 530 cm^{-1}, a region that is masked by several moderately intense bands of Tl_2O dimer.[14] On the other hand, if the 606-cm^{-1} band is assigned as the symmetric mode, the antisymmetric mode is calculated to lie near 1050 cm^{-1} and should be moderately intense (certainly more so than the 606-cm^{-1} band). No absorptions were noted in this region, despite a careful search. In addition, assignment of the 606-cm^{-1} band as the antisymmetric mode leads to a calculated ^{18}O shift of this mode of less than 1 cm^{-1}, while assignment as the symmetric C–S stretching mode leads to a calculated shift of 10 cm^{-1}. This latter shift should have been readily observed in the $Tl_2{}^{16}O/Tl_2{}^{18}O + CS_2$ experiment with band widths on the order of 1–2 cm^{-1}, yet no ^{18}O counterpart was observed (a weak band was noted at 574 cm^{-1}, but on the basis of magnitude of shift, band width, and intensity, this band cannot be assigned as the ^{18}O counterpart of the 606-cm^{-1} band). Consequently, assignment of the 606-cm^{-1} band to the antisymmetric C–S stretching mode of the $COS_2{}^{2-}$ anion is preferred, with the symmetric mode being less intense and likely obscured by the Tl_2O dimer bands in the 530-cm^{-1} region.

The two bands assigned here to the symmetric and antisymmetric S–C–S stretching modes in the $COS_2{}^{2-}$ anion lie at considerably lower energy than the analogous modes for the CS_2Se^{2-} anion in solution (840 and 925 cm^{-1}) and at somewhat lower than the analogous modes for dithiocarbomates[18] (for example, dimethyldithiocarbamate near 580 and 930 cm^{-1}). A rationale for this discrepancy is not readily apparent; the differences in electronic structure of the different species may be responsible. In addition, the physical environments are quite different, i.e. matrix-isolated ion triplet vs. ionic solution or crystalline solid. The spectra, however, demonstrate clearly that there were no ab-

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(17) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 3rd ed.; Wiley-Interscience: New York, 1978; p 130.

(18) Nieuwpoort, A.; Dix, A. H.; Porskamp, P. A. T. W.; ver der Linden, J. G. M. *Inorg. Chim. Acta* **1979**, *35*, 221.

Table I. Observed and Calculated Band Positions for the $Tl^+_2CO_2S^{2-}$ and $Tl^+_2COS_2^{2-}$ Triple Ions[a,b]

	CO_2S^{2-}		$C^{18}O_2S^{2-}$		$^{13}CO_2S^{2-}$	
assgnt	obsd	calcd	obsd	calcd	obsd	calcd
$\nu_4(B_1)$	1445.0	1440.7	1422.4	1427.6	1407.8	1403.7
$\nu_2(A_1)$	1202.0	1204.3	1197.6	1190.2	1173.4	1176.9
$\nu_1(A_1)$	602.8	603.8	602.6	596.1	602.6	599.2

	COS_2^{2-}		$C^{18}OS_2^{2-}$
	obsd	calcd	calcd
$\nu_1(A_1)$	1506.0	1503.9	1472.3
$\nu_4(B_1)$	606.8	608.9	608.9
$\nu_2(A_1)$		535.8	527.1

[a] Argon matrix frequencies. [b] Band positions in cm^{-1}.

sorptions in the 900-cm^{-1} region, and the assignments given above are preferred.

Normal-Coordinate Calculations

To support the assignments made above for both the CO_2S^{2-} and COS_2^{2-} anions and to provide an approximate force field for these species, normal-coordinate calculations were carried out, using a general valence force field. Bond lengths of 1.27 and 1.77 Å were used for the C–O and C–S bonds, respectively, and the geometry was fixed at C_{2v}. Since only stretching vibrations were observed for each anion, only approximate calculations could be carried out. These were done by omitting the bending and stretch–bend interaction force constants from the **F** matrix; clearly, this put a limitation on the final fit of observed vs. calculated frequencies. The alternative method of borrowing force constants from similar species could have been employed, but sufficiently little is known about such species that significant errors might occur. In addition, this approach would not allow for refinement, and since a number of isotopic bands were available for the CO_2S^{2-} anion, the former approach was adopted. For the CO_2S^{2-} anion a good fit was obtained with the primary force constants F_{C-O} = 6.85 mdyn/Å and F_{C-S} = 3.10 mdyn/Å. The average error for the nine observed frequencies was 4 cm^{-1}, which was quite acceptable within the approximations employed, as shown in Table I. The eigenvectors for these frequencies substantiated the nature of each of the vibrations as assigned above.

Two sets of calculations were conducted for the COS_2^{2-} anion; the first assigned the 606-cm^{-1} product band as the antisymmetric C–S stretch, while the second assigned this band as the symmetric C–S stretch. As noted above, the first calculation led to predictions more in accord with the observed spectrum and is the preferred assignment. The best fit was obtained with force constants F_{C-O} = 8.75 mdyn/Å and F_{C-S} = 2.45 mdyn/Å, although little refinement was possible due to the lack of isotopic data.

While the calculated force constants are limited by the approximations inherent in the calculations, some trends may be noted. F_{C-O} increased and F_{C-S} decreased on going from CO_2S^{2-} to COS_2^{2-}, which suggests that the carbon–oxygen bond takes on additional multiple-bond character in this latter anion while the carbon–sulfur bonds have less multiple-bond character. In fact, the calculated carbon–sulfur force constant is quite close to that for NCS^- anion, which contains (at least formally) a carbon–sulfur single bond. Hence, π-electron delocalization appears to diminish as sulfur is substituted for oxygen in these species, and the π-bonding becomes more localized in the carbon–oxygen bond, particularly for the COS_2^{2-} anion. Indeed, the C–O force constant for this species, 8.75 mdyn/Å, is quite typical of a carbon–oxygen double bond. These results are somewhat at odds with the most recent theoretical calculation,[6b] which predicted a contraction of both the carbon–oxygen and carbon–sulfur bond distances, along with an increase in both F_{C-O} *and* F_{C-S}. While there is no easy rationalization for this discrepancy, it should be noted that these ab initio calculations did not include d orbitals on the sulfur and in this regard alone must be regarded as approximate. Alternatively, the approximations, inherent in the above normal-coordinate calculations may be responsible, in particular the neglect of interaction between stretching and bending vibrations. However, previous calculations[11] on the carbonate anion have shown that the stretching frequencies, and hence force field, are relatively insensitive to stretch–bend interactions, and while this could contribute to the discrepancy in force fields, it is unlikely to be the entire cause.

Conclusions

The oxide-transfer technique, coupled with matrix isolation, has been employed for the synthesis of the mono- and dithiocarbonate anions CO_2S^{2-} and COS_2^{2-}, marking the first infrared spectroscopic observation of these species. For the monothiocarbonate anion, all three stretching vibrations were observed and both ^{13}C and ^{18}O data were obtained, while for the dithiocarbonate anion the carbon–oxygen and one of the carbon–sulfur stretching vibrations were observed. The observed frequencies were fit rather well by an abbreviated force field that included primary stretching force constants, as well as stretch–stretch interaction constants. The observed force constants suggest increased localization of the π bonding on the carbon–oxygen bond(s) as sulfur is substituted for oxygen in the sequence CO_3^{2-} to CS_3^{2-}.

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