Carbonates, Thiocarbonates, and the Corresponding Monoalkyl Derivatives. 1. Their Preparation and Isotropic ^{13}C NMR Chemical Shifts

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Three series of potassium carbonate and thiocarbonate salts were synthesized, and the corresponding ^{13}C isotropic solid-state NMR and the aqueous solution ^{13}C and ^{1}H NMR data were collected. The series of compounds that were studied consists of (1) the parent compounds, i.e., potassium carbonate, K_2CO_3, potassium hydrogen carbonate, $KHCO_3$, potassium monothiocarbonate, K_2CO_2S, potassium dithiocarbonate, K_2COS_2, and potassium trithiocarbonate, K_2CS_3, (2) the oxygen monoalkyl substituted derivatives of the parent compounds (OR series), i.e., three potassium *O*-alkylcarbonates, KO_2COR, three potassium *O*-alkylmonothiocarbonates, KOSCOR, and three potassium *O*-alkyldithiocarbonates, KS_2COR, all with R = CH_3, CH_2CH_3, $CH(CH_3)_2$, and (3) the sulfur monoalkyl substituted derivatives of the parent compounds (SR series), i.e., two potassium *S*-alkylmonothiocarbonates, KO_2CSR; two potassium *S*-alkyldithiocarbonates, KOSCSR, and two potassium *S*-alkyltrithiocarbonates, KS_2CSR, all with R = CH_3 or CH_2CH_3. The preparation and proper characterization of KO_2CSR and KOSCSR with R = CH_3 and CH_2CH_3 along with new IR and X-ray powder diffraction data for several other compounds in the series are reported for the first time in this study. Solution NMR data for KO_2CSR (R = CH_3, CH_2CH_3) and KOSCSR (R = CH_3) and solid-state NMR data for K_2CO_2S and K_2COS_2 could not be obtained because they are unstable under the corresponding measurement conditions. The isotropic chemical shift values of the central carbon atoms obtained from solid-state MAS (*m*agic *a*ngle *s*pinning) NMR experiments deviate at most by 3 ppm from the corresponding solution values. Two major trends in the ^{13}C chemical shift values of the central carbon atoms were found. First, if an oxygen atom in a parent compound or in an alkyl-substituted derivative is replaced by a sulfur atom, a significantly higher chemical shift value is observed. This trend is discussed in terms of the paramagnetic contribution to the chemical shielding constant. Second, the size of the alkyl group in the monoalkyl derivatives has a very small effect on the chemical shift values of the central carbon atoms. This observation is explained using the concept of varying inductive effects produced by alkyl groups. The trends observed for the ^{13}C and ^{1}H chemical shift values of the alkyl groups follow common concepts on the structure dependency of chemical shifts.

Introduction

The carbonates, thiocarbonates, and their corresponding monoalkyl derivatives were first investigated as early as 1850[1] and are, for the most part, well-studied compounds.[2] However, because of stability problems and difficulties in characterizing some of the compounds in solution and in the solid state, there is still much to be learned about their chemistry and about the chemistry of their decomposition products. ^{13}C NMR would seem to be ideally suited to the task of following the reactions of such compounds; however, isotropic chemical shift values of the carbonates, thiocarbonates, and their monoalkyl derivatives have not been systematically measured. The central purpose of this paper is to introduce new procedures for the synthesis of some of the compounds that have not been prepared and characterized previously and to record the ^{13}C and ^{1}H isotropic chemical shift data on the entire series of compounds. The chemical shift values have been, and will be, of value in developing the detailed chemistry of the carbonates and thiocarbonates in work yet to be published.

The chemical shift of the ^{13}C nucleus is due to a shielding effect produced by surrounding electrons. This shielding effect, expressed in the shielding constant σ, can be divided into an isotropic diamagnetic contribution and a paramagnetic contribution, designated with σ_d and σ_p, respectively.[3,4] Both terms arise from electronic currents induced by the external magnetic field; however, they are opposite in sign. The external field induces diamagnetic currents for all electrons. These diamagnetic currents produce shielding fields that oppose the external field, which means that an increase of this term results in a lower chemical shift. On the other hand, paramagnetic currents arising from electrons with intrinsic orbital angular momentum (i.e. p and d electrons) are also induced by the external field. These currents produce fields that add to the external field, and a

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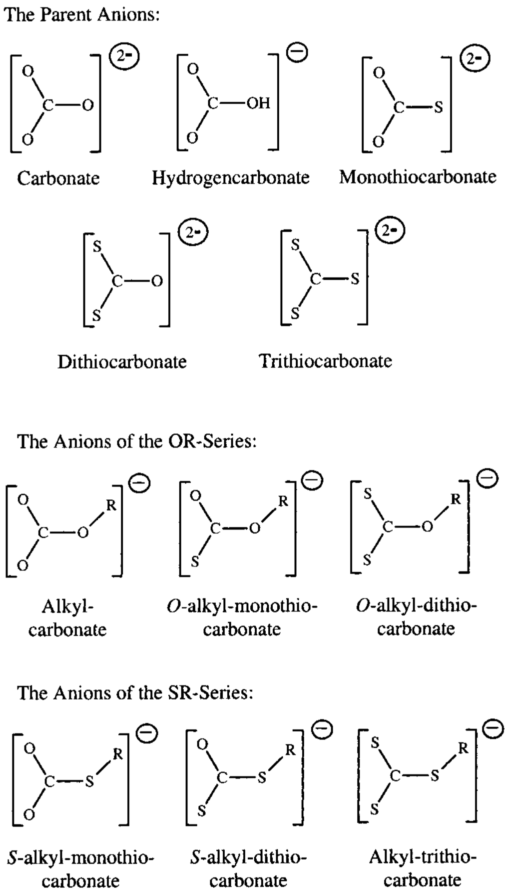

Figure 1. Nomenclature and σ-bond skeletons of the anions.

paramagnetic shift corresponds to deshielding of the nucleus. An increase of this term results in an increased chemical shift. Diamagnetic and paramagnetic shifts are comparable in magnitude. However, since diamagnetic shifts vary only approximately 5−10% for carbon atoms in different molecules with widely varying electronic structure, the relatively wide chemical shift range of approximately 400 ppm, observed for ^{13}C nuclei, is dominated by the highly variable paramagnetic shifts.[3,4] Another purpose of this study was to explore whether trends in the isotropic shielding values correlate with the bond structure around the central carbon atoms in the carbonates and thiocarbonates as oxygen atoms are systematically replaced with sulfur atoms. To obtain information about the electronic structure and the nature of the shielding processes present in the compounds studied, the shielding tensors and molecular orbitals for the parent anions and the monomethyl-substituted anions of the OR and SR series were calculated using ab initio quantum mechanical methods.

In this study, it was convenient to divide the compounds into three structurally related groups, i.e., the parent compounds, the OR series, and the SR series. Figure 1 shows the σ-bond skeletons of the anions in the three series and introduces the nomenclature. The parent compounds contain the nonsubstituted carbonate and thiocarbonate anions: potassium carbonate, K_2CO_3; potassium monothiocarbonate, K_2CO_2S; potassium dithiocarbonate, K_2COS_2; and potassium trithiocarbonate, K_2CS_3. Also included in the parent series is potassium hydrogen carbonate, $KHCO_3$. The members of the OR series have an alkyl group attached to an oxygen atom of the carbonate, monothio-, or dithiocarbonate anion. The members of the OR series included in this study are three potassium O-alkylcarbonates, KO_2COR, three potassium O-alkylmonothiocarbonates, KOSCOR, and three potassium O-alkyldithiocarbonates, KS_2COR. For all OR-series members the alkyl groups, R, were CH_3, CH_2CH_3, and $CH(CH_3)_2$. The members of the SR series have an alkyl group connected to one of the sulfur atoms of the mono-, di-, and trithiocarbonate anion. The members of the SR series included in this study are two potassium S-alkylmonothiocarbonates, KO_2CSR, two potassium S-alkyldithiocarbonates, KOSCSR, and two potassium S-alkyltrithiocarbonates, KS_2CSR. For all SR-series members the alkyl groups, R, were CH_3 and CH_2CH_3.

The carbonates and thiocarbonates can be prepared by following a general acid−base reaction pathway, which involves the reactions between the Lewis bases KOH, KSH, KOR, and KSR and the carbonic or thiocarbonic acid anhydrides CO_2, COS, and CS_2 as Lewis acids.[2] The individual chemical equations for the three series are (R = alkyl group) the following.

First Series

$$2KOH \xrightarrow{+CO_2} K_2CO_3 + H_2O \tag{1a}$$

$$\xrightarrow{+COS} K_2CO_2S + H_2O \tag{1b}$$

$$\xrightarrow{+CS_2} K_2COS_2 + H_2O \tag{1c}$$

$$2KSH \xrightarrow{+CS_2} K_2CS_3 + H_2O \tag{1d}$$

Second Series

$$KOR \xrightarrow{+CO_2} KO_2COR \tag{2a}$$

$$\xrightarrow{+COS} KOSCOR \tag{2b}$$

$$\xrightarrow{+CS_2} KS_2COR \tag{2c}$$

Third Series

$$KSR \xrightarrow{+CO_2} KO_2CSR \tag{3a}$$

$$\xrightarrow{+COS} KOSCSR \tag{3b}$$

$$\xrightarrow{+CS_2} KS_2CSR \tag{3c}$$

The end members of the parent compound series, potassium carbonate[5] and trithiocarbonate,[6] can be obtained as shown in eqs 1a and 1d. However, the anions of the two intermediate members of the series, the monothio- and dithiocarbonate anions, undergo competitive side reactions and are very unstable. Therefore, potassium monothio- and dithiocarbonate have not yet been prepared as pure materials.[7,8] In our study, the dithio- and monothiocarbonate anions were prepared, identified, and observed as unstable intermediates in strong alkaline, aqueous solutions at low temperatures. The procedure to prepare potassium trithiocarbonate given by Yeoman et al.[6] was slightly modified to obtain the parent compound in this study. The procedures to prepare the three members of the OR series, KO_2COR,[9] KOSCOR,[10,11] and KS_2COR,[12−15] as solids for a large

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variety of alkyl groups are well established in the literature.[2] As proposed in the literature, the reactions to prepare the OR-series compounds in this study were carried out by following the general reaction scheme described above in eqs 2a and 2b, but the exact experimental conditions differed in some cases. The preparation of $KS_2CSC_nH_{2n+1}$, containing several different alkyl groups with $n \geq 2$, using the approach described in eq 3c is reported in the literature.[16] Again, the experimental conditions for the syntheses of KS_2CSCH_3 and $KS_2CSCH_2CH_3$ in this study were altered from the procedures described in the literature.[16] The other two members of this series, KO_2CSR and KOSCSR, turned out to be very unstable, and procedures to synthesize these compounds have not been reported so far.[17] However, procedures to prepare the methyl- and ethylpotassium *S*-alkylmonothio- and dithiocarbonates as pure solids by following the reactions described in eqs 3a−3c were developed for the first time in this study. The IR data for $KO_2COCH(CH_3)_2$, KO_2CSCH_3, $KO_2CSCH_2CH_3$, $KOSCOCH(CH_3)_2$, $KOSCSCH_3$, $KOSCSCH_2CH_3$, and KS_2CSCH_3 also are reported herein for the first time.

Since K_2CO_2S and K_2COS_2 have not yet been prepared as solids and KO_2CSCH_3, $KO_2CSCH_2CH_3$, and $KOSCSCH_3$ decompose rapidly in aqueous solution, it is impossible to obtain complete solution and solid-state NMR data on all compounds. Similarly, the anions in KO_2COCH_3, $KO_2COCH_2CH_3$, $KO_2COCH(CH_3)_2$, and $KOSCSCH_2CH_3$ also decompose in aqueous solution. However, these decomposition reactions are relatively slow and the anions are present in solution long enough to obtain the corresponding chemical shift values. The recorded spectra show the peaks of the intact anions as well as the signals of their decomposition products.

Theoretical Calculations and Simulations

Chemical Shift Tensor Calculations. All calculations were performed on the isolated anions using the gauge invariant atomic orbital (GIAO) method[18] as implemented in the Gaussian 98[19] package. The shielding values for CO_3^{2-}, $O_2COCH_3^-$, $OSCOCH_3^-$, $S_2COCH_3^-$, $S_2CSCH_3^-$, and CS_3^{2-} [20] were calculated utilizing the B3P86[21,22]/aug-cc-pVTZ[23] level of theory[24] and using the experimental geometries as input files. Since X-ray data for CO_2S^{2-}, COS_2^{2-}, $O_2CSCH_3^-$, and $OSCSCH_3^-$ are not available in the literature, the geometries for these anions had to be obtained in optimization calculations. For this purpose, the HF/D95** [25] level of theory was utilized.[24] Subsequently, the shielding values were also calculated using the B3P86[21,22]/aug-cc-pVTZ[23] level of theory.

Simulation of the X-ray Powder Diffraction Spectra and Molecular Orbital Calculations. The X-ray powder diffraction patterns were simulated on the basis of the experimental X-ray structures of KO_2COCH_3,[26] $KOSCOCH_3$,[27,28] KS_2COCH_3,[29] $KS_2COCH_2CH_3$,[30] $KS_2COCH(CH_3)_2$,[31] and KS_2CSCH_3[32] using the Solids Builder package in the MSI[33] program. For sample characterization purposes these patterns were compared to the X-ray powder diffraction patterns that were recorded for these compounds in this study (see Experimental Section). The actual spectra are available upon request. The molecular orbital calculations were performed utilizing the MSI[33] program using the Dmol package at the BLYP[34,35]/minimum-basis level of theory.

Experimental Section

Solution NMR Experiments. All solution NMR measurements were performed on a Varian Inova 500 spectrometer. The ^{13}C spectra were acquired utilizing a 10 mm Nalorac broadband probe, and the ^1H spectra were recorded using a 5 mm Varian TRIAX probe. All spectra were acquired using 0.5 M solutions of the potassium compounds in D_2O at 25 °C and externally referenced to TMS using a capillary filled with neat liquid inserted in the NMR tube. Acquisition parameters were optimized for each experiment using a simple Bloch decay pulse sequence. Typical parameters were a spectral width of 41 kHz, a 90° pulse width of 8 μs, an acquisition time of 0.5 s, and a recycle delay of 10 s.

Solid-State NMR Experiments. The CPMAS and Bloch decay NMR experiments were performed on a Varian VXR-200 spectrometer, using a Doty Scientific 7 mm high-speed MAS probe. A standard cross polarization sequence and high-power proton decoupling were used to acquire the spectra, except for potassium carbonate and trithiocarbonate. The absence of protons in potassium carbonate and trithiocarbonate necessitated the use of Bloch decay methods. Typical parameters used for CP experiments were a spectral width of 20−40 kHz, a ^1H 90° pulse width of 4.0−4.5 μs, acquisition times between 100 and 150 ms, and recycle times between 5 and 10 s. Contact times were optimized on each sample and were found to vary between 5 and 8 ms. All spectra were recorded at room temperature and externally referenced to a CPMAS spectrum of hexamethylbenzene (HMB), with the methyl carbon taken to have a chemical shift of 17.6 ppm with respect to TMS.

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X-ray Powder Diffraction Spectra. The X-ray powder diffraction patterns were recorded on a RIGAKU diffractometer using a Cu radiation source. The scan range for 2θ was 5−50° at a step size of 0.083°/s.

IR Spectra. The IR spectra were recorded on the Perkin Elmer Paragon 1000PC FT-IR spectrometer in the range between 400 and 4000 cm^{-1} with a resolution of 4 cm^{-1}. All spectra were recorded on powdered or crystalline samples prepared as KBr pellets.

Materials. The liquid reactants and solvents (ethylmercaptan, carbon disulfide (CS_2), diethyl ether, acetone, ethanol, methanol, 2-propanol, tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), and methylene chloride (CH_2Cl_2)) were purchased from Aldrich as spectrophotometric grade materials. ^{13}C-labeled carbon disulfide ($^{13}CS_2$) was bought from Cambridge Isotope Laboratories, Inc. Potassium metal sticks of the highest available purity were purchased from Mallinckodt; potassium carbonate (C. P. grade) and potassium hydroxide (C. P. grade) were bought from Aldrich. The C. P. grade gaseous reactants, methylmercaptan, hydrogen sulfide (H_2S), carbonylsulfide (COS), and carbon dioxide (CO_2), were purchased from Matheson. The NMR solvents D_2O (99.9 atom % D) and tetramethylsilane (TMS) were also bought from Aldrich.

General Procedures. Potassium metal, potassium carbonate, and potassium hydroxide were stored and handled in an atmosphere of dry nitrogen. The solvents and liquid reactants as well as the gaseous reactants were dried over molecular sieves before use. Ethylmercaptan was further purified by refluxing for 4 h over potassium hydroxide before distilling onto molecular sieves. CS_2 was also distilled onto molecular sieves before use. COS was purified by passing it through a 1 M cadmium chloride solution before use to remove H_2S impurities. All reactions were carried out in oven-dried glassware under an atmosphere of nitrogen, which was dried over Drierite gas purifier and molecular sieves.

The potassium alkylthiolates were prepared in a 50 mL three-necked flask fitted with a condenser and a gas inlet by adding approximately 400 mg (0.0102 mol) of the metal to a 30 mL aliquot of the corresponding mercaptan while stirring and refluxing. During the reaction, ethylmercaptan was kept at 0 °C. Methylmercaptan was condensed into the flask at −80 °C, and the potassium was added at 0 °C. The condenser had to be additionally cooled from the outside with dry ice to avoid evaporation of the reactants. In both reactions a significant amount of hydrogen is evolved. The alkylthiolates form suspensions of white, powdered solids in the corresponding mercaptans.

In the syntheses of the *O*-alkyldithiocarbonates and the monoalkyltrithiocarbonates the respective solutions were saturated with CS_2 by connecting a wash-bottle containing approximately 10 mL of CS_2 into a nitrogen gas line, which was passed through the reaction mixture in the flask. The CS_2 was slowly carried into the reaction medium with the nitrogen gas stream.

Preparation of the Anions COS_2^{2-} and CO_2S^{2-} in Solution. CO_2S^{2-} and COS_2^{2-} were prepared by adding COS and CS_2, respectively, to a 2.5 mL sample of 8 M KOH solution in D_2O in a 10 mm NMR tube. CO_2S^{2-} was obtained by saturating the KOH solution with COS gas for 3 h at −30 °C, causing the clear and colorless KOH solution to turn slightly yellow. A capillary NMR tube, containing TMS as an external reference, was introduced into the NMR tube, which was subsequently sealed with a cap wrapped in Parafilm. A ^{13}C NMR spectrum of the solution at −10 °C was recorded.[36] COS_2^{2-} was obtained by adding a 0.39 mL aliquot of ^{13}C-labeled CS_2 (6.48×10^{-3}mol) to the KOH solution at −10 °C. The suspension was stirred for 4 h until all CS_2 had reacted. During that time period, the solution turned yellow but stayed clear. Again, a capillary NMR tube containing TMS as an external reference was introduced into the NMR tube, which was subsequently sealed as described above. A ^{13}C NMR spectrum of the solution at −10 °C was recorded.[36]

Preparation of K_2CS_3. A solution containing 7.84×10^{-3} mol of potassium ethoxide in 30 mL of ethanol was prepared as described above. In this synthesis the flask was also fitted with a drop funnel containing 5 mL of CS_2. The solution was warmed to 25 °C and saturated with H_2S for 2.5 h while stirring. The solution stayed clear and colorless. Subsequently, the solution was warmed to 45 °C and the CS_2 slowly added over approximately 30 min while stirring. The solution turned yellow with the first drop of CS_2, and after approximately 10 min fine pink crystals started to precipitate. During the 30 min the yellow color intensified and the amount of precipitate increased enormously. The suspension was stirred for another 1.5 h at 45 °C, subsequently cooled to 0 °C, and kept at that temperature for 1 h. The pink product was collected by filtration, washed three times with cold ethanol, and dried in a vacuum over P_2O_5 at 80 °C for a week. A 550.4 mg sample of K_2CS_3 in the form of very fine, pink crystals was obtained, which corresponds to a yield of 75.3%. The product was characterized by elemental analysis and IR spectroscopy. Anal. Calcd: 6.44% C, 41.96% K, 51.60% S. Found: 6.52% C, 41.52% K, 51.34% S. IR data for K_2CS_3 (KBr, cm^{-1}): lit.,[37] 900s; this study, 904s/sh, 886vs.

Preparation of KO_2COCH_3, $KO_2COCH_2CH_3$, and $KO_2COCH(CH_3)_2$. KO_2COCH_3, $KO_2COCH_2CH_3$, and $KO_2COCH(CH_3)_2$ were synthesized by following the procedures described in the literature[9] and were obtained as colorless needles in 93.6%, 94.3%, and 95.2% yields, respectively. The three compounds were characterized by IR spectroscopy. KO_2COCH_3 was also characterized by X-ray powder diffraction. IR data for KO_2COCH_3 (KBr, cm^{-1}): lit.,[9] 1689s, 1453s, 1435s, 1305s, 1185m, 1079s, 893s, 826s; this study, 1697s, 1455s, 1438s, 1307s, 1184m, 1080s, 893s, 824s. IR data for $KO_2COCH_2CH_3$ (KBr, cm^{-1}): lit.,[9] 2967s, 2907m, 1667s, 1389m, 1370s, 1295s, 1274m, 1114m, 1075m/sh, 1059s, 966s, 876s, 821s, 812m; this study, 2987m, 2974m, 1694vs, 1668vs, 1391m, 1371s, 1295s, 1114m, 1072s, 1060s, 966s, 875s, 821s, 812m/sh. IR data for $KO_2COCH(CH_3)_2$ (KBr, cm^{-1}): 2976s, 2942m, 2876w, 1666vs/br, 1622m/sh, 1470m, 1431m, 1445w, 1368vs, 1362vs, 1330s, 1303vs, 1287vs, 1175m, 1144m, 1120s, 1020vs, 1012vs, 908s, 847m, 825s, 715w, 579m, 466w.

Preparation of KO_2CSCH_3 and $KO_2CSCH_2CH_3$. Suspensions containing 4.03×10^{-3} mol of potassium methanethiolate in methylmercaptan and 5.89×10^{-3} mol of potassium ethanethiolate in ethylmercaptan were prepared as described above. The suspensions were saturated with CO_2 at 0 °C for 4 and 5 h, respectively, while stirring. During that time period, the amount of white precipitate increased noticeably in both syntheses. In the preparation of KO_2CSCH_3 the liquid methylmercaptan was evaporated by removing all cooling devices, passing a fast stream of dry nitrogen through the flask, and warming the reaction mixture to 30 °C while stirring. KO_2CSCH_3 remained in the flask as a white powder. It was collected and washed with diethyl ether. In the synthesis of $KO_2CSCH_2CH_3$, the white precipitate was separated by filtration and also washed with diethyl ether. Both products were dried in a vacuum over P_2O_5 at 30 °C for 3 days.[38] Obtained were a 471.4 mg sample of KO_2CSCH_3 in 89.8% yield and a 761.1 mg sample of $KO_2CSCH_2CH_3$ in 89.6% yield. Both products were characterized by elemental analysis and IR spectroscopy. Anal. Calcd for KO_2CSCH_3: 18.45% C, 2.33% H, 30.03% K, 24.63% S. Found: 18.32% C, 2.13% H, 30.17% K, 24.45% S. IR data for KO_2CSCH_3 (KBr, cm^{-1}): 2923m, 1617vs/b, 1578m/sh, 1452m/sh, 1420s, 1381m/sh, 1323vs, 1287vs, 1265vs, 808vs, 703s. Anal. Calcd for $KO_2CSCH_2CH_3$: 24.98% C, 3.50% H, 27.11% K, 22.29% S. Found: 24.87% C, 3.51% H, 26.92% K, 22.09% S. IR data for $KO_2CSCH_2CH_3$ (KBr, cm^{-1}): 2967m, 2930m, 2872m, 1593vs, 1454m, 1420s, 1406s/sh, 1317s, 1251s, 1055vw, 976w, 881w, 810s, 756w, 746w, 702s, 498w.

Preparation of $KOSCOCH_3$, $KOSCOCH_2CH_3$, and $KOSCOCH(CH_3)_2$. The three compounds were synthesized by following the general approach described in the literature.[10] However, in this study, the use of aqueous KOH solution was omitted and the reactions were conducted in the corresponding alcohols as solvents. Furthermore, the corresponding potassium alkoxides were prepared by adding potassium metal to the corresponding alcohol. $KOSCOCH_3$ was obtained as colorless

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(36) Since these compounds could not be isolated as solids, quantitative yields are not available.

(37) Mueller, A.; Mohan, N.; Cristophliemk, P.; Tossidis, I.; Draeger, M. *Spectrochim. Acta* **1973**, *29A*, 1345−1356.

(38) Attempts to recrystallize the *S*-alkylmonothiocarboantes in the same way as the *S*-alkyldithiocarbonates resulted in decomposition. However, recrystallization of the *S*-alkylmonothiocarboantes for purification purposes appeared to be unnecessary because the methods to characterize our samples indicate pure materials.

prism-shaped crystals in 91% yield, and $KOSCOCH_2CH_3$ and $KOSCOCH(CH_3)_2$ were obtained in the form of colorless needles in 93.4% and 94.2% yield, respectively. Since suitable single crystals of $KOSCOCH_3$ can be grown relatively easily by recrystalization from methanol, a complete X-ray structure determination was also performed. The derived structure agrees with the one obtained by Murphy et al.[27] and Gattow et.al.[28] However, because of more advanced techniques that are now available, the results obtained in our study are believed to be more accurate.[39] The actual data are available upon request. $KOSCOCH_3$ was also characterized by X-ray powder diffraction. IR data for $KOSCOCH_3$ (KBr, cm^{-1}): lit.,[40] 3020m, 3000m, 2940s, 1560vs/b, 1456m, 1438m, 1416s, 1385m, 1188m, 1090vs/b, 1048s, 965m, 812s, 695s, 532m, 423s; this study: 3022m, 3009m, 2950m, 1594vs/b, 1458m, 1423s, 1378m, 1186m, 1101vs/b, 1043s, 971m, 804s, 693m, 686m, 420s. IR data for $KOSCOCH_2CH_3$ (KBr, cm^{-1}): lit.,[40] 1585vs/b, 1474m, 1456m, 1444m, 1386m, 1358m, 1125s/sh, 1105vs/b, 1085s/sh, 1045s, 1030m, 840m, 692s; this study, 1591vs/b, 1479m, 1460m, 1447m, 1388m, 1359m, 1107vs/b, 1090vs/sh, 1046s, 1033m, 843m, 694s. IR data for $KOSCOCH(CH_3)_2$ (KBr, cm^{-1}): 2982s, 2976s/sh, 2934m, 2881m, 1590vs/b, 1486s, 1451m, 1386s, 1375s, 1343m, 1328m, 1178m/sh, 1145vs/sh, 1131vs, 1091vs/b, 920m, 841m, 693m, 435m.

Preparation of $KOSCSCH_3$ and $KOSCSCH_2CH_3$. Suspensions containing 4.03×10^{-3} mol of potassium methanethiolate in methylmercaptan and 6.16×10^{-3} mol of potassium ethanethiolate in ethylmercaptan were prepared as described above. The suspensions were saturated with COS at 0 °C for 4 and 5 h, respectively, while stirring. The amount of white precipitate increased noticeably in the course of both reactions. $KOSCSCH_3$ and $KOSCSCH_2CH_3$ were isolated in the same way as described above for KO_2CSCH_3 and $KO_2CSCH_2CH_3$, respectively. Subsequently, both products were recrystallized by the slow introduction of CH_2Cl_2 into a saturated solution of the materials in a 1:1 mixture of CH_2Cl_2 and DMF at 0 °C in a dry N_2 atmosphere and dried in a vacuum over P_2O_5 at 30 °C for 3 days. These procedures produced an 804.2 mg sample of $KOSCSCH_3$ in the form of very fine colorless needles in 92.7% yield and a 961.9 mg sample of $KOSCSCH_2CH_3$ also in the form of very fine colorless needles in a yield of 89.1%. Both products were characterized by elemental analysis and IR spectroscopy. Anal. Calcd for $KOSCSCH_3$: 16.42% C, 2.07% H, 26.73% K, 43.84% S. Found: 16.38% C, 2.00% H, 26.48% K, 43.69% S. IR data for $KOSCSCH_3$ (KBr, cm^{-1}): 2992m, 2918m, 1508vs/b, 1443s/sh, 1427s, 1418s/sh, 1299m, 1063m, 965vs, 891vs/b, 604m, 598m/sh. Anal. Calcd for $KOSCSCH_2CH_3$: 22.47% C, 3.15% H, 24.39% K, 40.00% S. Found: 22.12% C, 3.25% H, 24.56% K, 39.86% S. IR data for $KOSCSCH_2CH_3$ (KBr, cm^{-1}): 2981s, 2963s, 2923s, 2869m, 1561vs/b, 1451s, 1411s, 1373m, 1259m, 1052m, 1005m, 913vs, 866s/sh, 838m/sh, 588s.

Preparation of KS_2COCH_3, $KS_2COCH_2CH_3$, and $KS_2COCH(CH_3)_2$. The three compounds were synthesized by following the general approach described in the literature.[13] Again, in this study, the use of aqueous KOH solution was omitted, the reactions were conducted in the respective alcohols as solvents, and the corresponding potassium alkoxides were prepared by adding potassium metal to the corresponding alcohol. KS_2COCH_3, $KS_2COCH_2CH_3$, and $KS_2COCH(CH_3)_2$ were obtained as yellow needles in 94.3%, 92.3%, and 92.5% yield, respectively. IR data for KS_2COCH_3 (KBr, cm^{-1}): lit.,[41] 2932m, 1447m, 1430s, 1183vs, 1110vs, 1088s/sh, 1045vs, 477m; this study, 2933m, 1449m, 1430s, 1187vs, 1106vs, 1090s, 1048vs, 473m. NMR data for KS_2COCH_3 (^{13}C, CPMAS, ppm): lit.,[42] 235.4/233.6 (2:1 ratio), 62.8/61.7 (2:1); this study,[43] 235.6/235.1/233.5 (1:1:1), 62.6/61.4 (2:1). NMR (^{13}C, aqueous solution, ppm): lit,[42] 235.6, 62.4; this study, 233.6, 60.4.[44] IR data for $KS_2COCH_2CH_3$ (KBr, cm^{-1}): lit.,[45] 1145vs, 1122vs, 1107vs, 1055vs, 1015s, 447m; this study, 1144vs/b, 1119s, 1100vs/b, 1051s, 1008vs, 447s. IR data for $KS_2COCH(CH_3)_2$ (KBr, cm^{-1}): lit.,[46] 1470s, 1380m, 1186s, 1151s, 1133s, 1080vs/b; this study, 1384m, 1371vs, 1184vs, 1149vs, 1130vs, 1061vs/vb. NMR data for $KS_2COCH(CH_3)_2$ (^{13}C, CPMAS, ppm): lit,[42] 232.4, 78.6/77.0 (1:1), 23.0/22.2(broad) (1:2); this study, 232.8, 79.1/77.4 (1:1), 23.4/22.8/22.5 (1:2:3). NMR (^{13}C, aqueous solution, ppm): lit.,[42] 235.1, 81.0, 23.9; this study, 232.0, 78.0, 20.8.[44] KS_2COCH_3, $KS_2COCH_2CH_3$, and $KS_2COCH(CH_3)_2$ were also characterized by X-ray powder diffraction.

Table 1. Isotropic ^{13}C Solid-State MAS and Solution Chemical Shift Values for the Parent Compounds[a]

compound	MAS[b]	solution[c]
$KHCO_3$	162.0	160.4
K_2CO_3	171.2	168.3
K_2CO_2S	*d*	186.4
K_2COS_2	*d*	222.1
K_2CS_3	270.8	269.6

[a] All values are given in ppm. [b] All spectra were recorded at room temperature and externally referenced to a CPMAS spectrum of hexamethylbenzene (HMB), with the methyl carbon taken to have a chemical shift of 17.6 ppm with respect to TMS. [c] Solution spectra were recorded at room temperature in 0.5 M D_2O solutions with neat TMS as the external standard. [d] Chemical shift value could not be obtained because of chemical instability under the measurement conditions.

Preparation of KS_2CSCH_3 and $KS_2CSCH_2CH_3$. Suspensions containing 6.01×10^{-3} mol of potassium methanethiolate in methylmercaptan and 6.81×10^{-3} mol of potassium ethanethiolate in ethylmercaptan were prepared as described above. Both suspensions were saturated with CS_2 at 0 °C for 4 h as described above. In the course of the both reactions the white potassium alkylthiolate slowly disappeared and KS_2CSCH_3 and $KS_2CSCH_2CH_3$ gradually began to precipitate as bright-yellow amorphous solids. Both products were isolated in the same way as described above for KO_2CSCH_3 and $KO_2CSCH_2CH_3$ (the CS_2 was evaporated with the methylmercaptan) and subsequently recrystallized by the slow introduction of diethyl ether into a saturated solution of the materials in a 1:1 mixture of diethyl ether and THF at 0 °C in a dry N_2 atmosphere. After both products were dried in a vacuum over P_2O_5 at 50 °C for 3 days, an 899.0 mg sample of KS_2CSCH_3 in the form of prism-shaped bright-yellow crystals in 92.3% yield and a 1.0981 g sample of $KS_2CSCH_2CH_3$ in the form of fine bright-yellow needles in 91.5% yield were obtained. Single crystals of KS_2CSCH_3 suitable for an X-ray structure analysis were grown, and a complete structure determination was performed.[32] IR data for KS_2CSCH_3 (KBr, cm^{-1}): 1012vs, 940m, 847s, 830s, 795m/sh. IR data for $KS_2CSCH_2CH_3$ (KBr, cm^{-1}): lit.,[47] 1050s, 1000vs, 850s, 840s/sh, 740m; this study, 1048vs, 1000vs, 991vs, 854s, 841s, 744m. KS_2CSCH_3 was also characterized by X-ray powder diffraction.

Results

NMR Data. The ^{13}C isotropic solid-state and solution chemical shift values for all carbon atoms in the compounds studied are presented in Tables 1−3. Multiple chemical shift values in the MAS column for solid samples indicate the presence of magnetically nonequivalent carbon atoms in the crystal unit cell. This observation is in agreement with X-ray structure determinations performed on the potassium *O*-alkyldithiocarbonates KS_2COCH_3,[29] $KS_2COCH_2CH_3$,[30] and $KS_2COCH(CH_3)_2$.[31] X-ray data to confirm the presence of magneti-

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(39) The standard deviations for cell dimensions and atomic positions are smaller in this study. Furthermore, the *R* factor and the higher number of independent reflections used indicate a more accurate structure determination.

(40) Mattes, R.; Scholten, K. *Spectrochim. Acta* **1975**, *31A*, 1307−1315.

(41) Colthup, N. B.; Powell, L. P. *Spectrochim. Acta* **1987**, *43A*, 317−322.

(42) Hounslow, A. M.; Lincoln, S. F.; Tiekink, E. R. T. *J. Chem. Soc., Dalton Trans.* **1989**, 233−236.

(43) The three magnetically nonequivalent central carbon atoms were resolved in this study.

(44) Small deviations in the measured chemical shift values are probably due to differences in concentrations used in the measurements and/or different reference methods.

(45) Little, L. H.; Poling, G. W.; Leja, J. *Can. J. Chem.* **1961**, *39*, 745−754.

(46) Pearson, F. G.; Stasiak, R. B. *Appl. Spectrosc.* **1958**, *12*, 116−120.

(47) Pelizzi, G. C.; Pelizzi, C. *Inorg. Chim. Acta* **1970**, *4*, 618−620.

Table 2. Isotropic ^{13}C Solid-State CPMAS and Solution Chemical Shift Values for the Members of the OR Series[a]

compound	carbon atom	MAS[b]	solution[c]
KO_2COCH_3	$O_2\mathbf{C}O$	159.6	160.2
	$\mathbf{C}H_3$	54.0	53.2
$KO_2COCH_2CH_3$	$O_2\mathbf{C}O$	158.8	159.7
	$\mathbf{C}H_2$	60.9	62.0
	$\mathbf{C}H_3$	16.1	14.8
$KO_2COCH(CH_3)_2$	$O_2\mathbf{C}O$	158.7/157.8	159.3
	$\mathbf{C}H$	68.4/67.7	69.1
	$\mathbf{C}H_3$	24.2/23.7/22.1	21.6
$KOSCOCH_3$	$O_2\mathbf{C}O$	185.8	186.1
	$\mathbf{C}H_3$	56.9	53.4
$KOSCOCH_2CH_3$	$O_2\mathbf{C}O$	187.5	185.5
	$\mathbf{C}H_2$	63.4	62.8
	$\mathbf{C}H_3$	15.9	13.7
$KOSCOCH(CH_3)_2$	$O_2\mathbf{C}O$	186.8	185.1
	$\mathbf{C}H$	70.1	70.4
	$\mathbf{C}H_3$	24.1/22.2	21.3
KS_2COCH_3	$O_2\mathbf{C}O$	235.6/235.1/233.5	233.6
	$\mathbf{C}H_3$	62.6/61.4	60.4
$KS_2COCH_2CH_3$	$O_2\mathbf{C}O$	234.0/232.4	232.8
	$\mathbf{C}H_2$	73.6/72.7	70.3
	$\mathbf{C}H_3$	16.5/16.1	13.6
$KS_2COCH(CH_3)_2$	$O_2\mathbf{C}O$	233.4	232.0
	$\mathbf{C}H$	79.6/78.0	78.0
	$\mathbf{C}H_3$	24.0/23.4/23.1	20.8

[a] All values are given in ppm [b] All spectra were recorded at room temperature and externally referenced to a CPMAS spectrum of hexamethylbenzene (HMB), with the methyl carbon taken to have a chemical shift of 17.6 ppm with respect to TMS. Multiple chemical values indicate the presence of magnetically nonequivalent carbon atoms in the crystal unit cell. [c] Solution spectra were recorded at room temperature in 0.5 M D_2O solutions with neat TMS as the external standard.

Table 3. Isotropic ^{13}C Solid-State CPMAS and Solution Chemical Shift Values for the Members of the SR Series[a]

compound	carbon atom	MAS[b]	solution[c]
KO_2CSCH_3	$O_2\mathbf{C}O$	173.5	*d*
	$\mathbf{C}H_3$	18.3	
$KO_2CSCH_2CH_3$	$O_2\mathbf{C}O$	173.8	*d*
	$\mathbf{C}H_2$	29.2	
	$\mathbf{C}H_3$	15.9	
$KOSCSCH_3$	$O_2\mathbf{C}O$	209.6	*d*
	$\mathbf{C}H_3$	19.5	
$KOSCSCH_2CH_3$	$O_2\mathbf{C}O$	203.7	205.9
	$\mathbf{C}H_2$	28.9	27.1
	$\mathbf{C}H_3$	17.6	14.2
KS_2CSCH_3	$O_2\mathbf{C}O$	247.4	248.6
	$\mathbf{C}H_3$	25.8	24.6
$KS_2CSCH_2CH_3$	$O_2\mathbf{C}O$	247.8	247.5
	$\mathbf{C}H_2$	39.2	35.5
	$\mathbf{C}H_3$	13.3	12.5

[a] All values are given in ppm. [b] All spectra were recorded at room temperature and externally referenced to a CPMAS spectrum of hexamethylbenzene (HMB), with the methyl carbon taken to have a chemical shift of 17.6 ppm with respect to TMS. [c] Solution spectra were recorded at room temperature in 0.5 M D_2O solutions with neat TMS as the external standard. [d] Chemical shift value could not be obtained because of chemical instability under the measurement conditions.

Table 4. Proton Solution NMR Data of the Protons in the Alkyl Groups[a]

compound	proton	δ[b]	*J*
KO_2COCH_3	$C\mathbf{H}_3$	2.86 (s)	
$KO_2COCH_2CH_3$	$C\mathbf{H}_2$	3.26 (q)	7.2
	$C\mathbf{H}_3$	0.52 (t)	
$KO_2COCH(CH_3)_2$	$C\mathbf{H}$	3.87 (sp)	6.0
	$C\mathbf{H}_3$	0.51 (d)	
$KOSCOCH_3$	$C\mathbf{H}_3$	2.92 (s)	
$KOSCOCH_2CH_3$	$C\mathbf{H}_2$	3.37 (q)	7.2
	$C\mathbf{H}_3$	0.53 (t)	
$KOSCOCH(CH_3)_2$	$C\mathbf{H}$	4.18 (sp)	6.0
	$C\mathbf{H}_3$	0.53 (d)	
KS_2COCH_3	$C\mathbf{H}_3$	3.34 (s)	
$KS_2COCH_2CH_3$	$C\mathbf{H}_2$	3.80 (q)	7.2
	$C\mathbf{H}_3$	0.68 (t)	
$KS_2COCH(CH_3)_2$	$C\mathbf{H}$	4.85 (sp)	6.4
	$C\mathbf{H}_3$	0.66 (d)	
KO_2CSCH_3	$C\mathbf{H}_3$	*c*	
$KO_2CSCH_2CH_3$	$C\mathbf{H}_2$	*c*	*c*
	$C\mathbf{H}_3$		
$KOSCSCH_3$	$C\mathbf{H}_3$	*c*	
$KOSCSCH_2CH_3$	$C\mathbf{H}_2$	2.05	7.6
	$C\mathbf{H}_3$	0.51	
KS_2CSCH_3	$C\mathbf{H}_3$	1.94 (s)	
$KS_2CSCH_2CH_3$	$C\mathbf{H}_2$	2.51 (q)	7.5
	$C\mathbf{H}_3$	0.61 (t)	

[a] Chemical shift values δ are given in ppm, and coupling constants *J* are given in Hz. [b] Solution spectra were recorded at room temperature in 0.5 M D_2O solutions with neat TMS as the external standard. Multiplicity of the observed proton resonance is given in parentheses after the chemical shift values. Abbreviations stand for the following: s = singlet, d = doublet, t = triplet, and sp = septet. [c] Value could not be obtained because of chemical instability under the measurement conditions.

cally nonequivalent carbon atoms in $KO_2COCH(CH_3)_2$ and $KOSCOCH(CH_3)_2$ are not available. However, the solid-state MAS spectra of these two compounds clearly show nonequivalencies for some of the carbon atoms. The nonequivalencies are eliminated in solution by random molecular motion. The values listed in Tables 1−3 reveal that the differences between the solution chemical shift values and the isotropic solid-state chemical shift values obtained in the MAS experiments are relatively small. They follow no obvious trend and vary only within ±3 ppm. This suggests that solid-state and solution values can be used interchangeably for discussing major chemical shift trends.

Table 4 shows the proton aqueous solution chemical shift values and the corresponding coupling constants for the compounds of the OR and SR series.

Trends in the ^{13}C and ^{1}H Chemical Shift Values of the Alkyl Groups. The carbon atoms and protons in methylene groups attached to an oxygen or sulfur atom show higher chemical shifts than the carbons in methyl groups. Furthermore, chemical shift values are higher for methoxy and CH_2 ethoxy carbon atoms and the attached protons, compared to the corresponding sulfur-containing groups. All these observations are in agreement with common concepts on the structure dependency of chemical shifts.[48]

Effects of Different Alkyl Groups on the ^{13}C Chemical Shift Values of the Central Carbons. The effect of the alkyl group on the chemical shift of the central carbon atoms is only systematic for the chemical shift values measured in solution. Figure 3 shows a plot of the available solution chemical shift values versus the different alkyl groups that were investigated. Also included in the plot is the chemical shift value for $KHCO_3$, in which R = H. Linear fits of the data points reveal slopes and R^2 values of -1.10 and 1.0000 for S_2CSR^-, -0.80 and 1.0000 for S_2COR^-, -0.50 and 0.9868 for $OSCOR^-$, and -0.38 and 0.9757 for O_2COR^-, respectively. It is evident that there is a slight linear decrease in the chemical shift values as the alkyl groups become larger. Further, the effect is more pronounced as the number of sulfur atoms in the anions increases.

Effect of Replacing Oxygen Atoms with Sulfur Atoms on the ^{13}C Chemical Shift Values. The average ^{13}C chemical shift

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(48) Günther, H. *NMR Spektroskopie, 3. neubearbeitete und erweiterte Auflage*; Georg Thieme Verlag: New York, 1992.

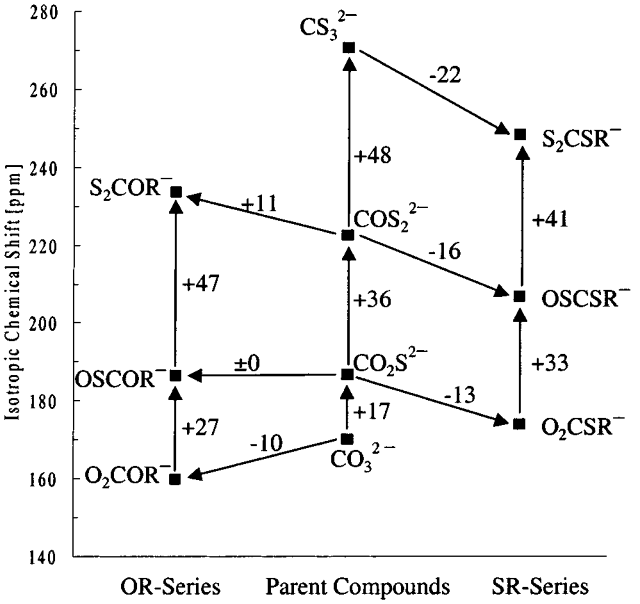


Figure 2. Trends of the averaged isotropic chemical shift values of central carbon atoms in the three series.

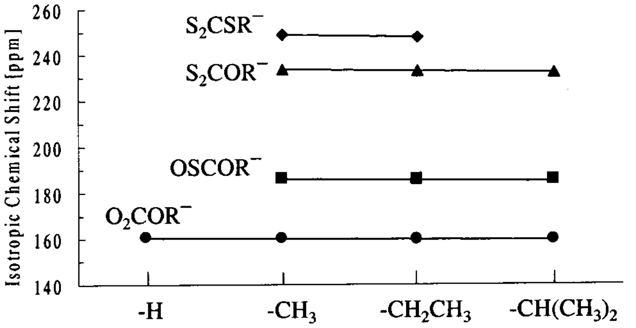


Figure 3. Effect of different alkyl groups on the solution chemical shift values of the central carbon atoms.

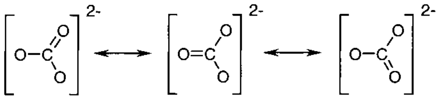
values[49] of the central carbon atoms are presented in a schematic form in Figure 2. The figure reveals trends within each of the three series as well as relative trends between the series. A trend observed within all three series is that the isotropic chemical shift value of the central carbon atom increases dramatically when an oxygen atom in an anion is replaced by a sulfur atom. The trend of increasing chemical shift appears to be slightly nonlinear within the SR series but is strongly nonlinear within the OR series and the parent compounds series. Figure 2 further shows that all the central carbons in the three members of the SR series are found to have chemical shift values lower than in the corresponding parent compounds. The magnitude of this reduction in chemical shift increases when more sulfur atoms are present in the corresponding parent anion. The OR series shows completely different behavior. Adding a methyl group to the carbonate anion results in a decrease in chemical shift, adding a methyl group to the monothiocarbonate anion produces virtually no change in chemical shift, and adding a methyl group to the dithiocarbonate anion leads to an increase in chemical shift.

Discussion

Change in the ^{13}C Chemical Shift Values of the Central Carbon Atoms Produced by the Alkyl Groups. The trend that is produced by the alkyl groups is consistent with the general organic postulate that the ability of an alkyl group to donate electrons, i.e., the inductive effect (+I effect), increases with its size.[50,51] It is also consistent with the premise that the inductive effect is transmitted more effectively through more polarizable (more deformable or "softer") atoms.[50,51]

An increasing +I effect is assumed to result in a greater σ-electron density at the carbon nucleus, which would result in a more shielded ^{13}C nucleus and would cause a decrease in the chemical shift (diamagnetic shift). It has to be emphasized, however, that the changes are small and differences are near the limit of detection. The reason for the barely detectable +I effect of the alkyl groups can probably be attributed to the fact that the groups are not directly bonded to the carbon atom of interest; rather, the effect is transmitted through an additional atom. Nevertheless, the consistency of the data supports the conclusion that the small differences are real and are consistent with conventional charge polarization concepts. The isotropic solid-state NMR data of the central carbon atoms do not show a systematic trend related to the size of different alkyl groups. This might be attributed to the fact that strong Coulomb interactions in the ionic crystals mask the relatively weak +I effect of the different alkyl groups. These interactions are averaged through fast molecular motion in solution.

Change in the ^{13}C Chemical Shift of the Central Carbon Atoms when Oxygen Atoms Are Systematically Replaced by Sulfur Atoms. Carbonates have been written with resonating multiple bonds since the concept was formulated in the early electronic models of Pauling,[52] resulting in familiar presentations such as the following:



Each oxygen atom is bound by a partial π bond. The resonating structure requires the carbonate ion to be planar (sp^2 hybridization of the carbon atom) with bond angles of 120° and three equal C−O bond distances.[52,53] Experimental data on calcite and other carbonates reveal distances in the range between 1.29 and 1.31 Å and angles between 118° and 122°.[53,54] While the existence of a C−O multiple bond is generally accepted, the case for a C−S multiple bond encounters considerable controversy. Although the C−S double bond has been proposed, the degree of overlap of a large sulfur 3p orbital with a small carbon 2p orbital is small, resulting in a very weak π interaction. In 1964 Roberts and Caserio[55] pointed out the weakness of 2p−3p π bonds involving carbon bound to sulfur, phosphorus, or silicon. These authors reported that only unstable compounds are known with C=Si, C=P, and C=S bonds in which the S, P, or Si atoms utilize 3p orbitals in π-bond overlap. They further noted that an S−O π-type bond could be considered in which an unshared electron pair on the oxygen could interact with d orbitals of the sulfur atom. However, this is very different from the linkage implied by the C=S notation. The Roberts and

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(49) An average of the solid-state and solution chemical shift values for each series member is displayed.

(50) Neckers, D. C.; Doyle, M. P. *Organic Chemistry*; Wiley & Sons: New York, 1977; pp 399, 458−461.

(51) Roberts, J. D.; Caserio, M. C. *Basic Principles of Organic Chemistry*; Benjamin, Inc.: New York, 1965; pp 515−517, 551, 956.

(52) Pauling, L. *Nature of the Chemical Bond*, 2nd ed.; Cornell University Press: Ithaca, NY, 1942; p 208.

(53) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, 1984; p 920.

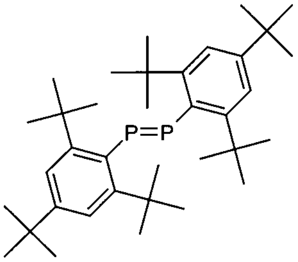
(54) Sass, A. L.; et al. *Acta Crystallogr.* **1957**, *10*, 567.

(55) Roberts, J. D.; Caserio, M. C. *Basic Principles of Organic Chemistry*; Benjamin, Inc.: New York, 1965; p 745.

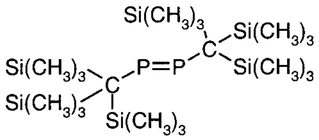
Caserio linkage is more closely related to those suggested for molecules such as SF_6.

For many years, inorganic chemists have rationalized differences in physical properties of nitrogen (N_2) compared to phosphorus (molecular structures of P_4 (white) and P_n (red and other modifications)) and of oxygen (O_2) compared to sulfur (molecular structures of S_8 and S_n). O_2 and N_2 are gases containing strong multiple π bonds, whereas the low multiple bonding capability of P and S makes their dimeric structures unstable relative to the extended polymerized structures. Before 1981, this belief was summarized in the classical double bond rule. The rule was given in the statement "Elements which have a principal quantum number greater than 2 should not be able to form a double bond (or multiple σ plus π, etc.) with themselves or other elements."[56]

In 1981, a valid exception to the "double bond rule" was reported by Yeshifuji, Shima, Inamoto, Hirotsu, and Higutchi at the International Phosphorus Symposium at Duke University:[57,58,59]



This compound contains very bulky 2,4,6-tri-*tert*-butylphenyl groups, which effectively block the normal formation of a polymeric species. A very similar species was reported by Cowley and associates in 1982:[60]


$$[(CH_3)_3Si]_2(Si(CH_3)_3)C{-}P{=}P{-}C[Si(CH_3)_3]_3$$

The stabilities of the double-bonded compounds described in this work are ascribable to the kinetic stabilization afforded by the sterically demanding substituents. The writing of a double bond in these and related structures was questioned by Pauling,[61] but many of the parameters associated with a double bond appear in these highly sterically hindered systems. The bottom line seems to be that multiple bonds linking elements involving electrons with a quantum number $n \geq 2$ are considered stable only in highly sterically hindered molecules.

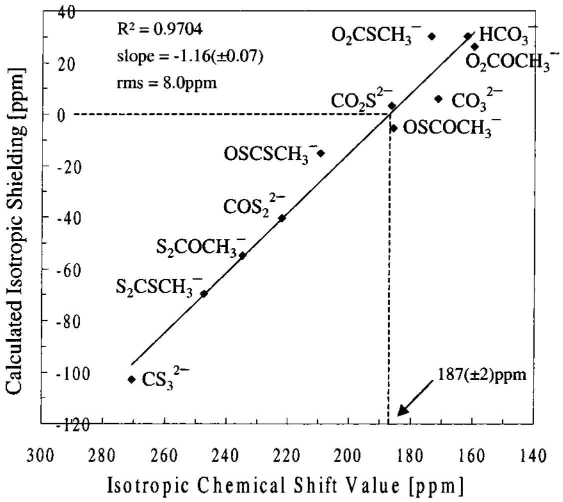


Figure 4. Correlation between the calculated shielding values of the central carbon atoms and the corresponding experimental chemical shift values.

The evaluation of the isotropic ^{13}C NMR data of the carbonates and thiocarbonates collected in this study supports the postulates made in the previous paragraphs about weak π interactions between second- and third-row elements. The trends observed for the isotropic chemical shift values of the central carbon atoms in the anions predict C−S 2p−3p π bonds to be very weak compared to much stronger C−O 2p−2p π bonds. Figure 4 shows a plot of the calculated isotropic shielding values of the central carbon atoms of the parent anions and the monomethyl-substituted anions versus the corresponding experimental chemical shift values. The slope, R^2 value, and standard deviation for a linear fit of the data are also displayed in the figure and reveal a good correlation. The slope of the line is nearly −1.00, indicating that the calculated shielding changes are in good agreement with the observed chemical shift changes as sulfur is substituted for oxygen. The zero point on the shielding scale corresponds to the bare nucleus or the point where the diamagnetic and paramagnetic contributions exactly cancel. This point also corresponds to a chemical shift value of 187 ± 2 ppm, as indicated in Figure 4 by the dotted line and the arrow next to the chemical shift axis. The plot further shows that the anions $OSCOCH_3^-$, $OSCSCH_3^-$, COS_2^{2-}, $S_2COCH_3^-$, $S_2CSCH_3^-$, and CS_3^{2-} have paramagnetic components that exceed the diamagnetic terms, producing chemical shifts higher than the shift of 187 ppm for a bare nucleus. The deshielding of the ^{13}C nucleus when oxygen atoms are replaced with sulfur atoms can be primarily attributed to a significant increase in the paramagnetic shift term. Theory predicts that the paramagnetic shift term for the ^{13}C nucleus is determined by[4] (1) the inverse of the composite energy separations, $1/\Delta E$, between the ground state and all excited states, (2) the relative electron densities in the various p orbitals involved in bonding, and (3) the value of the average inverse cube distance from the nucleus to the orbitals involved. The plot in Figure 5 shows the correlation between the calculated shielding values and $1/\Delta E$ values extracted from the molecular orbital calculations, using the differences between the HOMOs and LUMOs in the anions. Again, the parameters for a linear fit of the data are given in the figure. The excellent correlation suggests that the $1/\Delta E$ dependency most likely dominates the paramagnetic shielding term. The plot shows a decrease in the energy separation between the HOMOs and LUMOs when oxygen atoms are successively replaced with sulfur atoms. Such lower excitation energies are characteristic of weak bonds, lending experimental support for the postulate that a C−S π interaction is relatively weak because of a poor overlap between carbon 2p and sulfur 3p orbitals compared to a strong C−O π interaction involving carbon 2p and oxygen 2p orbitals.[55,56] The constitution of a C=S

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(56) Cowley, A. H.; Kilduff, J. E.; Newman, T. H.; Pakulski, M. J. *J. Am. Chem. Soc.* **1982**, *104*, 5820−5821.

(57) Yeshifuji, M.; Shima, I.; Inamoto, N. In *Proceedings of the 1981 International Conference on Phosphorus Chemistry*; Quin, L. D., Verkade, J. G., Eds.; ACS Symposium Series 171; American Chemical Society: Washington, DC, 1981.

(58) Yeshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587−4589.

(59) Yeshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1982**, *104*, 6167.

(60) Cowley, A. H.; Kilduff, J. E.; Lasch, J. G.; Mehrotra, S. K.; Norman, N. C.; Pakulski, M.; Whittlesey, B. R.; Atwood, J. L.; Hunder, W. E. *Inorg. Chem.* **1984**, *23*, 2582−2593 (see p 2591).

(61) Pauling, L. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 3871.

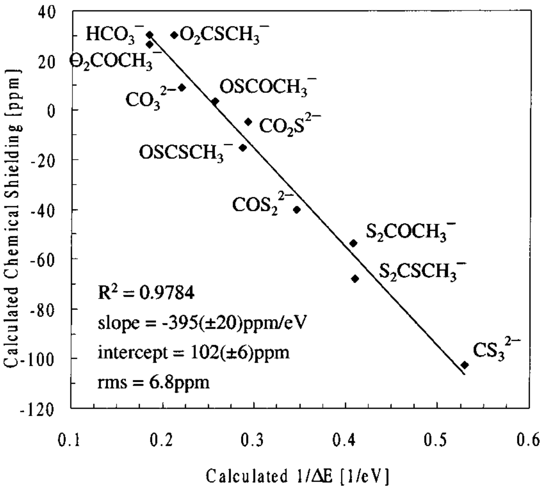

Figure 5. Correlation between the calculated shielding values of the central carbon atoms and the inverse of the energy separation between the LUMOs and HOMOs in the anions.

π bond is a matter of degree and not an either/or proposition, and C−S π bonding is very weak at best but not negligible. Steric protection of such weak electronic interactions explains the observations by Higutchi et al.[58,59] and by Cowley et al.[60]

The ^{13}C chemical shift values of the central carbon atoms in 26 different dialkyl carbonates and thiocarbonates (RX(CY)-ZR, with R = alkyl group and X, Y, Z = O, S) including a variety of different alkyl groups were examined by Copeland et.al.[62] These compounds are closely related to the parent compound and the corresponding monomethyl derivatives studied here. The chemical shift values obtained in our study are in agreement with the results published by Copeland et al. Both data sets show an increase of the chemical shifts of the central carbon atoms upon replacement of oxygen with sulfur atoms and reveal only minor effects of the alkyl groups on the chemical shifts of the central carbon atoms. Furthermore, Copeland et al. discovered that two different types of substitutions in the dialkyl series result in two different chemical shift trends of the central carbon atoms. The replacement of an oxygen atom in an alkoxy group to yield a thioalkoxy group (type 1) results in an increase in chemical shift between 10 and 20 ppm, whereas the alternative replacement of an oxygen atom involved in π bonding (type 2) causes the chemical shift to increase between 36 and 46 ppm. These two types of substitutions discovered by Copeland et al. can also be found in the OR and SR series. A type 1 substitution corresponds to an oxygen substitution in a member of the OR series to give the member of the SR series with the same number of sulfur atoms and causes chemical shift changes between 14 and 21 ppm (see chemical shift values in Tables 2 and 3). A type 2 substitution relates consecutive members in the OR and SR series and produces chemical shift changes between 27 and 47 ppm (see scheme in Figure 2). Copeland et al. refer to the explanation given by Demarco et al.[63] to account for the trends observed for the dialkylcarbonates and thiocarbonates in terms of a lower mean excitation energy, ΔE, for weak C−S π bonds compared to stronger C−O π bonds, resulting in a larger paramagnetic shielding term. This is in agreement with the interpretations made in our study as stated above.

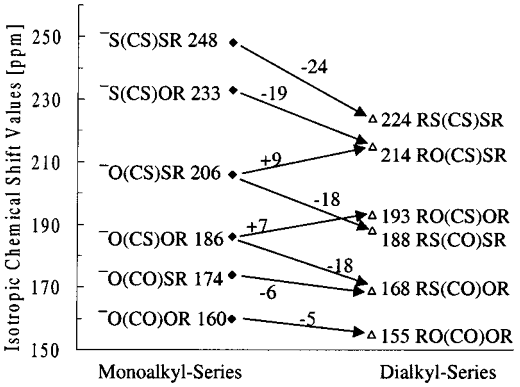

Figure 6. Relative trends in the averaged isotropic chemical shift values between the monoalkyl- and dialkylcarbonates and thiocarbonates.

Combining the data collected by Copeland et al. and the data obtained in this study allows the evaluation of the relative trends in the chemical shift values of the central carbon atoms between the monoalkyl and dialkyl carbonates and thiocarbonates. Both data sets are displayed in Figure 6. Labeled arrows indicate the change in chemical shift when a second alkyl group in a monoalkyl compound is added to an oxygen or a sulfur atom and depict the resulting dialkyl compound. The figure reveals that adding an alkyl group to a sulfur atom in S_2CSR^- and S_2COR^- or an oxygen atom in O_2CSR^- and O_2COR^- always results in a decrease in chemical shift. This decrease is approximately 4 times larger for S_2CSR^- and S_2COR^-. In $OSCSR^-$ and $OSCOR^-$ an oxygen and a sulfur atom are available for an addition and different effects are observed. Adding an alkyl group to an oxygen atom in these two anions increases the chemical shift by a few ppm, whereas adding it to a sulfur atom causes the chemical shift to decrease by approximately twice that amount. The trends observed between the monoalkyl and dialkyl carbonates and thiocarbonates are consistent with the trends revealed in our study and by Copeland et al. for the individual series, respectively, and confirm the general observation that higher chemical shifts are observed as more sulfur atoms are attached to the central carbon atoms.

Conclusions

The members of the potassium carbonate−trithiocarbonates series, as well as several corresponding *O*- and *S*-monoalkyl derivatives, were prepared and characterized. Isotropic ^{13}C and ^{1}H NMR chemical shift values were measured for all compounds that are stable under the measurement conditions and are reported here.

The trend that the isotropic ^{13}C chemical shift values of the central carbon atoms increase upon substitution of oxygen atoms with sulfur atoms observed in our study is in agreement with data previously obtained by Copeland et al. on a related series of compounds and can be interpreted in terms of the paramagnetic contribution to the chemical shielding constant. Linear correlations between the calculated chemical shielding values and the experimental isotropic chemical shift values verify that the theoretical structural modeling of the chemical shift produces a faithful representation. The contribution to the paramagnetic shielding term, σ_p, appears to be dominated by the inverse of the varying energy separations between the HOMOs and LUMOs. The energy separations between the HOMOs and LUMOs in the anions decrease when oxygen atoms are successively replaced with sulfur atoms. Lower excitation energies are characteristic of weak bonds, and the measurement of increasing chemical shift values when more sulfur atoms are

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(62) Copeland, C.; Conway, R. J.; Patroni, J. J.; Stick, R. V. *Aust. J. Chem.* **1981**, *34*, 555−557.

(63) Demarco, P. V.; Doddrell, D.; Wenkert, E. *Chem. Commun.* **1969**, 1418−1420.

present in the anions therefore supports the existence of only weak C−S π interactions compared to strong C−O π interactions.

The effect of the different alkyl groups on the chemical shift values of the central carbon atoms in the monoalkyl compounds in aqueous solution is very small but nevertheless detectable. It can be rationalized by employing the concept of an increase in the +I effect as the size of the alkyl group increases.

Adding an alkyl group to the oxygen atoms in CO_3^{2-}, CO_2S^{2-}, and COS_2^{2-} causes a decrease, no change, and an increase in the chemical shift of the central carbon atoms, respectively. On the other hand, when alkyl groups are added to sulfur atoms in CO_2S^{2-}, COS_2^{2-}, and CS_3^{2-}, only a decrease in the chemical shift values of the central carbon atoms is produced.

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