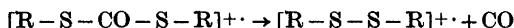


Mass Spectra of Some Simple *O,S*- and *S,S*-Dialkyl Dithiocarbonates

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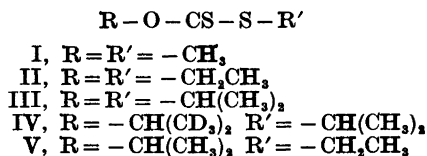
The mass spectra of some simple *O,S*- and *S,S*-dialkyl dithiocarbonates are reported and discussed. Reaction mechanisms for the decompositions of the ionized compounds have been studied by means of exact mass measurements and deuterium labelling. The amount of kinetic energy released in the process



has been measured.

In connection with an investigation of the thermal and electron-impact-induced fragmentations of bis(alkoxythiocarbonyl) disulfides knowledge about the mass spectrometric behaviour of simple *O,S*- and *S,S*-dialkyl dithiocarbonates was required.¹ Whereas the mass spectra of *O,S*- and *S,S*-aryl alkyl and diaryl dithiocarbonate have been subject to extensive investigation,^{2,3} nothing has to our knowledge been published about the corresponding dialkyl compounds except for a detailed report on the electron-impact-induced fragmentations of *S*-methyl *O*-(2-methylcyclohexyl) dithiocarbonate and deuterated analogues.⁴ The mass spectra of various dialkyl- and diaryl-carbonates have been published.⁵

O,S-Dialkyl dithiocarbonates. The mass spectra of five *O,S*-dialkyl dithiocarbonates (I-V) were recorded (Fig. 1).



These mass spectra are characterized by peaks corresponding to α -cleavages and McLafferty rearrangements. All spectra contain abundant peaks due to the alkyl ions.

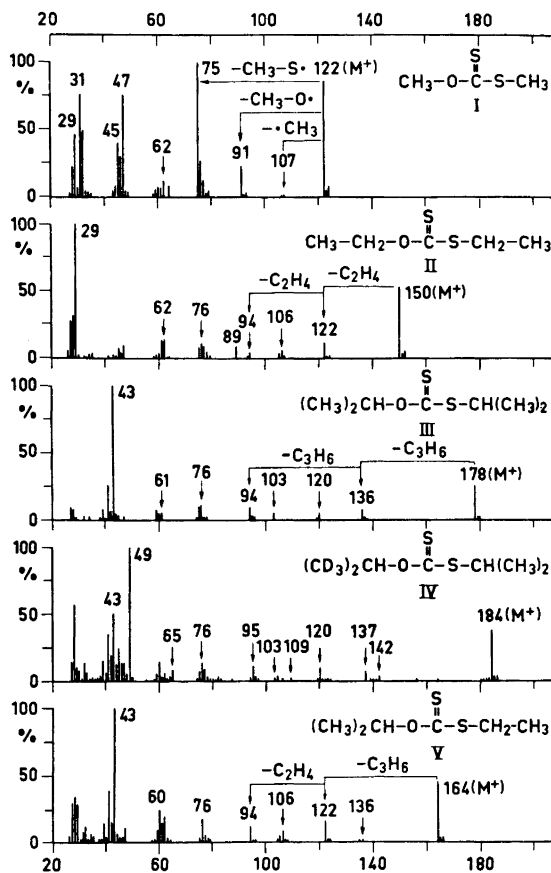
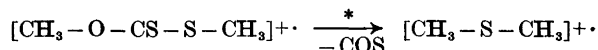


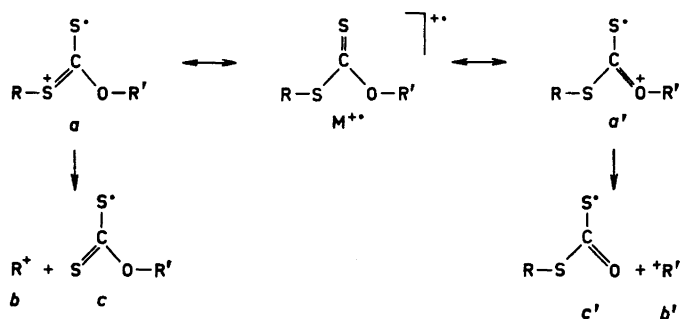
Fig. 1.

Dimethyl dithiocarbonate (I) is unable to undergo McLafferty rearrangement, and the two α -cleavage reactions become very important. Since the stability of the $\text{CH}_3-\text{S}^\cdot$ radical exceeds that of the $\text{CH}_3-\text{O}^\cdot$ radical, the $\text{M}-\text{CH}_3\text{S}$ ions are much more abundant than the $\text{M}-\text{CH}_3\text{O}$ ions. The mass spectrum of (I) also contains prominent peaks at m/e 47, 45, 31, and 29 corresponding to CH_3S^+ , CHS^+ , CH_3O^+ , and CHO^+ , respectively. Abundant peaks corresponding to similar ions were not found in the mass spectra of the remaining compounds (II–V). Finally the mass spectrum of (I) contains a peak at m/e 62, due to ionized dimethyl sulfide.



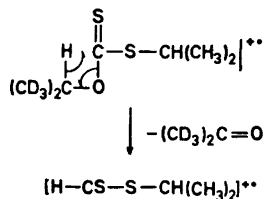
A similar skeletal rearrangement has been reported for the aromatic analogues,^{2,3} whereas this process is not observed for the higher homologues of this series.

The base peaks in the mass spectra of the remaining compounds (II–V) are due to the alkyl ions. From the mass spectrum of IV it is seen that the formation of $(\text{CD}_3)_2\text{CH}^+$ is nearly twice as favourable as the formation of $(\text{CH}_3)_2\text{CH}^+$. In terms of bond energies the $\text{S}-\text{CH}(\text{CH}_3)_2$ bond is weaker than the $\text{O}-\text{CH}(\text{CD}_3)_2$ bond, so that the $\text{C}-\text{S}$ bond should be more easily cleaved. If, however, the molecule possesses a sufficient amount of excess energy this factor becomes unimportant. Most cleavage reactions have at 70 eV rates determined by the frequency factor.⁶ If the frequency factors for these two processes are approximated by the $\text{C}-\text{O}$ and $\text{C}-\text{S}$ stretching frequencies, which are of the order of 1100 and 700 cm^{-1} , respectively, a ratio of 2:1.3 for the $(\text{CD}_3)_2\text{CH}^+ / (\text{CH}_3)_2\text{CH}^+$ ions can be calculated in good agreement with the observed 2:1 ratio. However, this approach does not take into account the influence of the resonance structures a and a' on the $\text{R}-\text{S}$ and $\text{R}-\text{O}$ stretching frequencies.



The McLafferty rearrangements give rise to peaks corresponding to $[\text{R}-\text{O}-\text{CS}-\text{SH}]^{+\bullet}$, $[\text{HS}-\text{CO}-\text{S}-\text{R}]^{+\bullet}$ and $[\text{HO}-\text{CS}-\text{SH}]^{+\bullet}$ (or $[\text{HS}-\text{CO}-\text{SH}]^{+\bullet}$). It is evident from the mass spectrum of the deuterated compound (IV) that the molecular ion undergoes the rearrangement primarily with participation of the *O*-alkyl group. In the mass spectrum of (V) this tendency is even more pronounced, probably due to the fact that the *O*-alkyl group ($-\text{CH}(\text{CH}_3)_2$) in this case is larger than the *S*-alkyl ($-\text{C}_2\text{H}_5$).

Whereas the mass spectrum of (I) displays peaks due to α -cleavages with loss of $\text{CH}_3\text{S}^\bullet$ as well as $\text{CH}_3\text{O}^\bullet$, the remaining mass spectra display peaks corresponding to $\text{M}-\text{RO}^\bullet + \text{H}^+$. In the mass spectra of III and IV the peaks corresponding to this process are found at m/e 120, indicating that the hydrogen transferred comes from the α -carbon. The mechanism can be depicted as:



S,S-Dialkyl dithiocarbonates. Four *S,S*-dialkyl dithiocarbonates (VI–IX) have been investigated.

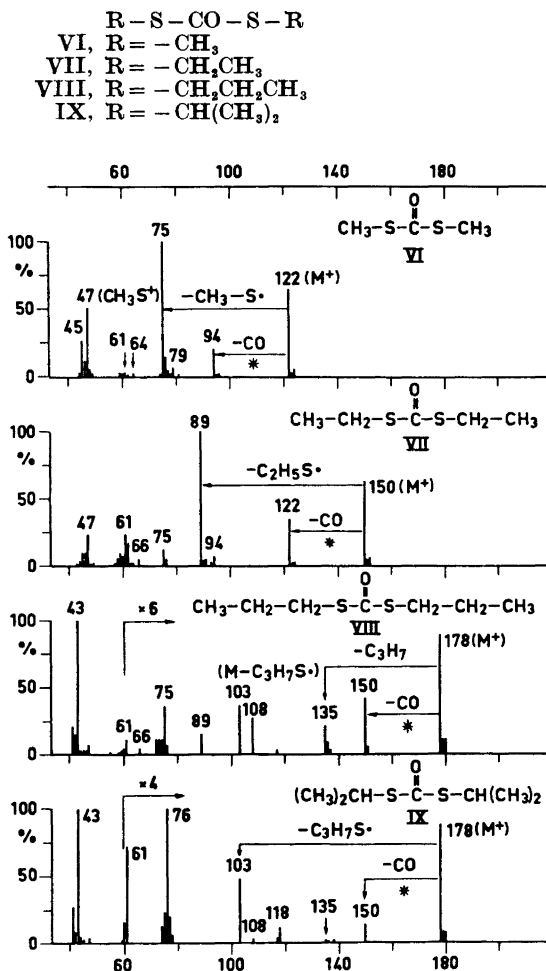


Fig. 2.

The mass spectra of these compounds differ from those of the *O,S*-isomer by the presence of $M - \text{CO}$ peaks and the absence of peaks corresponding to a McLafferty rearrangement of the molecular ion. Hence, isomeric *O,S*- and *S,S*-dialkyl dithiocarbonates can easily be distinguished by means of mass spectrometry.

Loss of carbon monoxide from the molecular ion of *S*-phenyl *S*-methyl dithiocarbonate leading to ionized methyl phenyl disulfide has been reported.^{2,3} In the mass spectra of these compounds (VI–IX) the corresponding metastable

peaks at $(M - 28)^2/M$ are "flattopped", indicating the release of kinetic energy.⁷ For the four compounds the amount of kinetic energy released was determined and the following figures found: CH_3 0.47 eV; C_2H_5 0.57 eV; $\text{CH}_3\text{CH}_2\text{CH}_2$ 0.28 eV; $(\text{CH}_3)_2\text{CH}$ 0.17 eV.

The electron-impact-induced fragmentations and rearrangements of dialkyl disulfides have been investigated,⁸ and the reported decompositions were also found here. (For $\text{R} = -\text{CH}_3$: m/e 79, 64, 61, and 45. For $\text{R} = -\text{C}_2\text{H}_5$: m/e 94 and 66. For $\text{R} = -\text{C}_3\text{H}_7$: m/e 108 and 66.)

In all four cases α -cleavages give rise to abundant $\text{M} - \text{RS}'$ as well as RS'^+ peaks.

Loss of one alkyl group from the molecular ion is important only in the case of VIII ($\text{R} = -\text{CH}_2\text{CH}_2\text{CH}_3$). The mass spectrum of compound IX ($\text{R} = -\text{CH}(\text{CH}_3)_2$) contains two abundant peaks at m/e 76 and 61 corresponding to $(\text{CH}_3)_2\text{CH} - \text{SH}^+$ and $\text{CH}_3 - \text{CH} = \text{SH}^+$. As the samples employed were shown to be pure by GLC the formation of $(\text{CH}_3)_2\text{CH} - \text{SH}^+$ can only be due to electron-impact-induced fragmentation of IX and not to contamination of the sample.

EXPERIMENTAL

The mass spectra were recorded at an AEI MS902 mass spectrometer using the all glass inlet. All compounds investigated were submitted to gas chromatography and elemental analysis to check their purity.

O,S-Dialkyl dithiocarbonates were prepared by alkylating the sodium alkyl xanthate, ROCSSNa , with the appropriate alkyl halide.^{9a} Compounds IV and V have not been described previously and were prepared with acetone as solvent in the following way: Sodium alkylxanthate (0.01 mol) (prepared from the alcohol, sodium hydride, and carbon disulfide) was dissolved in dry acetone (20 ml), alkyl iodide (0.01 mol) added, and the mixture refluxed for 15 min. The reaction mixture was concentrated *in vacuo* at room temperature and the product extracted with ether. After washing with water the ether extract was dried over anhydrous magnesium sulfate and the ether removed *in vacuo*. The resulting ester was distilled *in vacuo* and the material boiling over a small interval was used for the mass spectroscopic analysis. IV, b.p. 43–44°C (0.3 mm); V, b.p. 83.5–84°C (16 mm).

S,S-Dialkyl dithiocarbonates were obtained from the sodium thiolate and phosgene as described.^{9b}

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