Formation of a Two-centre, Three-electron, Sulphur–Sulphur Bond in the Gas Phase

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The dimer formed in the gas-phase reaction of ionized di-isopropyl sulphide with its neutral analogue is shown to possess a strong sulphur–sulphur bond.

Continuing interest in two-centre, three-electron bonds, as exemplified by the simple sulphur[1] (**1**) and nitrogen[2] (**2**) containing examples,[3] has focused on developing methods for

$$\left.\mathrm{H_2S\therefore SH_2}\right]^{+\bullet} \qquad (\mathbf{1})$$

$$\left.\mathrm{H_3N\therefore NH_3}\right]^{+\bullet} \qquad (\mathbf{2})$$

characterizing these systems. However, except for an *X*-ray crystallographic study of the cation radical of 1,6-diazabicyclo-[4.4.4]tetradecane showing the molecular arrangement around the two nitrogen atoms and suggesting intramolecular N–N bonding,[4] the majority of the methods have been indirect, involving estimation of the energy gap between σ-bonding and σ-antibonding levels by optical spectroscopy,[3] e.s.r. spectroscopy,[5] or ejection of the electron in the antibonding level *via* charge-stripping mass spectroscopy.[6] Bonding between the two heteroatom centres has been inferred from experimental evidence and substantiated primarily by *ab initio* MO calculations. However, actual bonding, for example where two molecular units are joined by a two-centre, three-electron bond to form a unique, isolable, molecular entity has, strictly speaking, never been demonstrated. Furthermore, thermodynamic data are sparse. Estimates of the bond energy for (**1**) range from *ca.* 70 to 120 kJ $\mathrm{mol^{-1}}$, and energies are believed to be as high as 240 kJ $\mathrm{mol^{-1}}$ for the S–S cases in disulphides.[7] An unambiguous method to prove experimentally the existence of such species and to measure their thermodynamic properties would be of great utility for the understanding of these systems. Gas-phase generation and characterization would be particularly useful, as under these conditions the effects of solvent and counterions are not operative.

In this communication we describe for the first time the generation of a two-centre, three-electron sulphur–sulphur bond; the ionic species are formed in a bimolecular reaction in the gas phase, and characterized by both Fourier transform ion cyclotron resonance (FTICR)[8] and tandem mass spectrometry (MSMS).[9]

Generation of stable charged dimers in the gas phase under low pressure conditions is difficult since the encounter complexes are thermally isolated. As a consequence, the gained ion/dipole energy is dissipated in the adduct ion and, as a rule, drives a reaction of the adduct ion to products or back

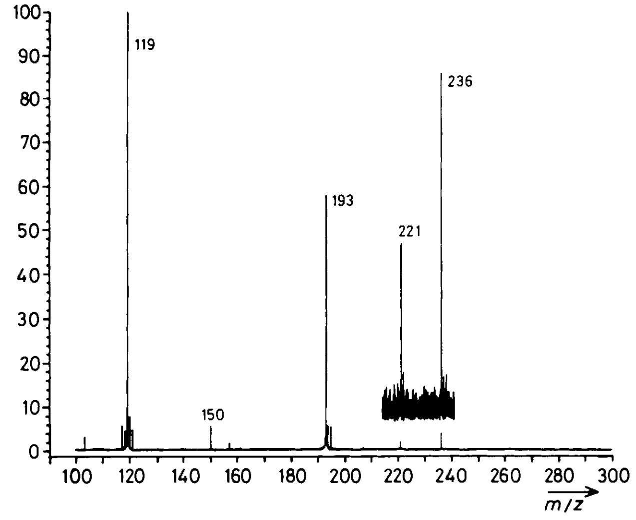


Figure 1. The FTICR spectrum (Bruker CMS 47) of di-isopropyl sulphide (1.3×10^{-6} mbar) after a reaction time of 2 s during which a 20 ms pulsed-valve addition of helium buffer gas (up to *ca.* 10^{-4} mbar) was applied.

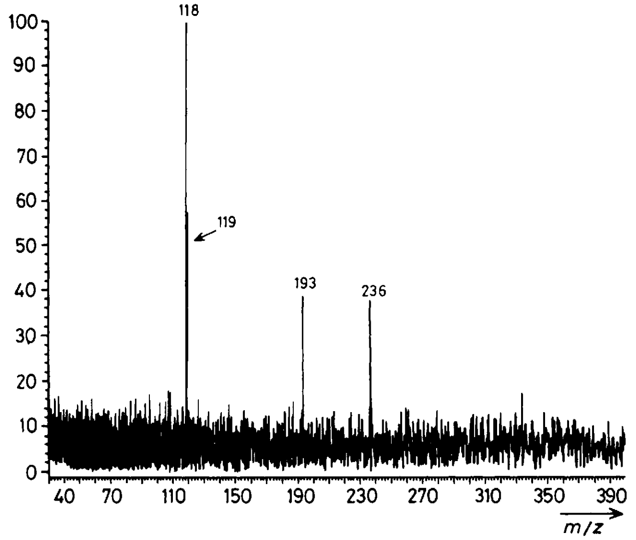


Figure 2. Collisional induced fragmentation (FTICR) of the di-isopropyl sulphide cation dimer. The dimer was isolated by ejection of all other ions from the cell, translationally excited, and then allowed to collide with newly pulsed-in He gas (*ca.* 10^{-4} mbar).

to reactants. However, the lifetime of the encounter complex can be increased by increasing the molecular size so that the excess energy can be accommodated by dispersion to the vibrational modes of the complex. We have employed this concept by using di-isopropyl sulphide as substrate; in this system some of the adduct ions have sufficiently long lifetimes for collisional deactivation to take place during a pulsed valve addition of the buffer gas. This appeared essential in the FTICR experiments (performed on the Bruker CMS 47 instrument at the University of Amsterdam[10]).

When di-isopropyl sulphide was ionized in the FTICR cell and allowed to react for 2 s in the presence of a pulsed He buffer gas (up to *ca.* 10^{-4} mbar), a signal corresponding to the dimer was observed (Figure 1; *m/z* 236). Its identity is confirmed by the isotopic abundance expected for molecules containing two sulphur atoms. In order to examine whether this dimer was bound by loose ion/dipole interactions or by a true covalent sulphur–sulphur bond, the ionized di-isopropyl sulphide dimer was selected by ejecting all other ions from the cell, translationally excited and then brought into collision with newly pulsed helium gas. The resulting collisional activation spectrum (Figure 2) shows the expected charged monomer (*m/z* 118) accompanied by the protonated monomer (*m/z* 119). An additional signal at *m/z* 193 corresponds to the loss of an isopropyl radical, suggesting S–C cleavage.

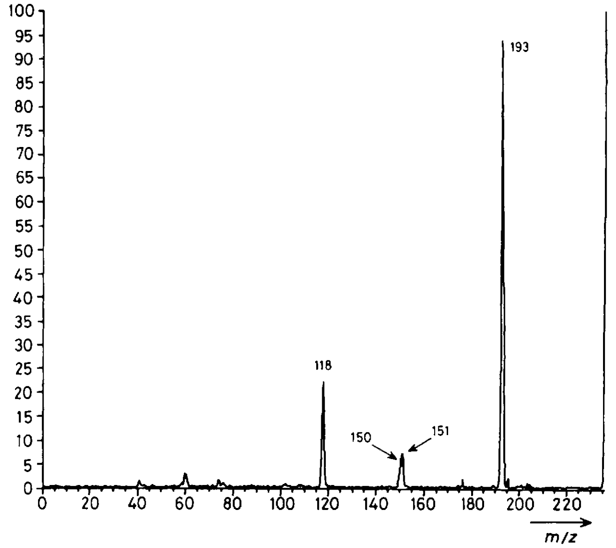
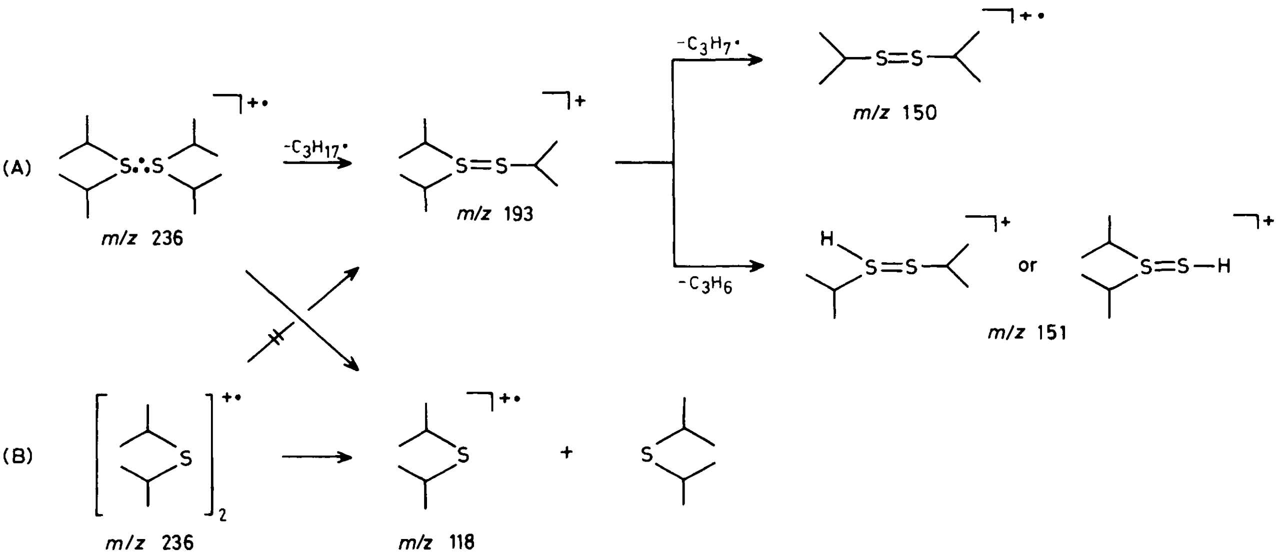


Figure 3. Collisional induced fragmentation spectrum of the di-isopropyl sulphide cation dimer (ZAB-HF-3F). The ion was formed in a chemical ionization source (*ca.* 10^{-4} mbar), mass selected with the magnet of the first sector, and brought into collision with He (5×10^{-6} mbar) in the second field-free region. The fragment ions were detected by scanning the ESA.

An analogous experiment, performed on the Vacuum Generator triple mass spectrometer (ZAB-HF-3F) at the Technical University of Berlin, yielded similar results (Figure 3). However, the signal due to isopropyl radical loss was much stronger and the protonated monomer was not observed. This suggests that the signal at *m/z* 119 of Figure 2 is due to some secondary reactions during collisional activation in the FTICR resulting in the protonation of a neutral sulphide. However, since the collision energy in the FTICR experiment is lower by a factor of about 100 than in the ZAB experiment, the formation of the protonated monomer is perhaps better explained as a collision-induced protonation reaction within the complex, followed by fragmentation. The signals at *m/z* 150 and 151 (Figure 3) are due to losses of $C_3H_7^{\cdot}$ and C_3H_6, respectively, from the species *m/z* 193 [reaction (A)].

The loss of the isopropyl radical, proceeding probably *via* reaction (A), indicates that the strength of the S–S bond in the dimer is of the same order of magnitude as that of the S–C bond. An ion/dipole complex would be expected to yield only the charged monomer, *via* reaction (B). Similar behaviour, *i.e.* cleavages of the S–C bonds, has also been suggested in the solution phase, where rearranged isomers of similar dimers were obtained.[11] The loss of the isopropyl radical thus indicates that the three-electron sulphur–sulphur bond is quite strong, perhaps of the same magnitude as a normal S–C bond (280 kJ mol^{-1} for the neutral species). However, the strength of the S–S bond of the dimer is probably less than that of the neutral S–C bond, since the S–C bond of the cation radical is weaker than that of the corresponding neutral species.



Attempts were made (by FTICR) to generate nitrogen and mixed nitrogen–sulphur dimers, which are believed to form two-centre, three-electron bonds in solution. These attempts failed, probably because the amino group is too basic, and as a consequence only protonated monomers and dimers were observed.

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