

THE ION TRAP MASS SPECTRUM OF SULFUR

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(Received 28 March 1990)

ABSTRACT

The mass spectrum of sulfur (S_8) obtained with the ion trap mass spectrometer is compared with that obtained using an E-B spectrometer. Each ion in the spectrum is examined for fragmentation and the vapor shown to consist mostly of the S_8 oligomer. The chemical ionization spectra using methane, isobutane, ammonia, and water are also examined and an estimate made of the proton affinity of S_8 . Using methane, most of the fragment ions are derived from $(M + C_2H_5)^+$ rather than $(M + H)^+$.

INTRODUCTION

One of the many uses of MS is the determination of the degree of oligomerization of compounds and elements. However, when the substance being examined tends to depolymerize under the spectrometer source conditions, analysis of the oligomer content may become difficult. Two principle factors causing depolymerization in electron impact spectrometers are electron energy and the heat required for volatilization of the sample. Lowering the electron energy may allow separation of these effects but a price in sensitivity will be exacted; furthermore, except for the use of metastable peaks, it is often difficult to determine the depolymerization pathway. Chemical ionization (CI) mass spectrometry, with its reduced tendency to fragment ions while retaining sensitivity [1], can usefully replace electron impact in such analyses while tandem techniques (MS-MS) [2] are particularly helpful in fragmentation studies.

Elemental sulfur is a classic example of a compound undergoing such oligomerization. Its tendency to catenate and form large rings from S_2 - S_{20} is well known and considered to relate to its use of $4s$ and $3d$ orbitals [3]. This

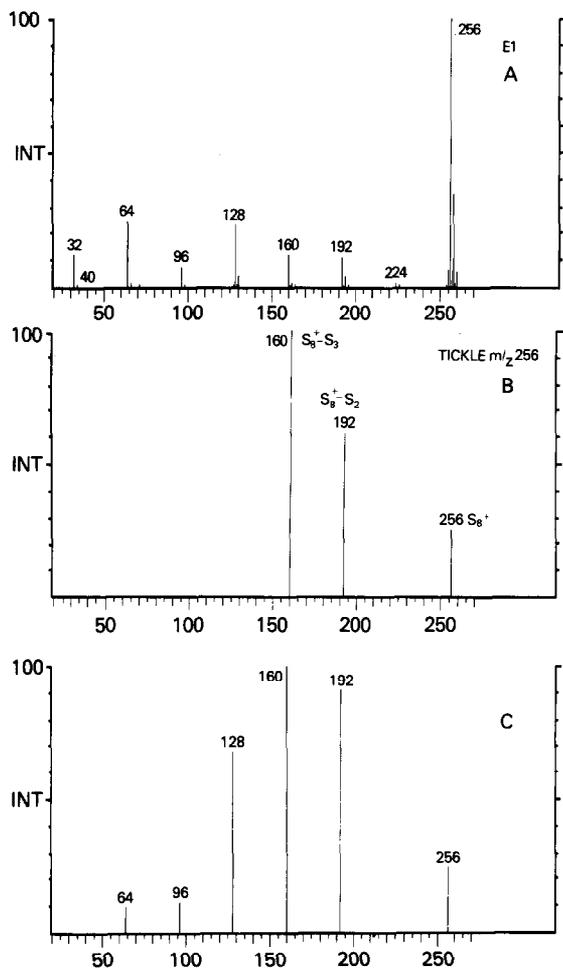


Fig. 1. (A) Electron impact mass spectrum of S₈ obtained with the ITMS at 150°C. (B) MS-MS of *m/z* 256 of S₈⁺ obtained with the ITMS. (C) MS-MS spectrum of *m/z* 256 of S₈⁺ redrawn from ref. 8.

tendency extends even to many of its combined forms and many organic and inorganic polysulfides are known. Because of the way the commonly encountered oligomer (S₈) mimics many organic compounds in solubility and appearance, its EI spectrum (Fig. 1A) is well known in many analytical laboratories. The actual number of oligomeric species in the vapor above elemental sulfur that contribute to this spectrum has been the subject of several studies [3-7]. In a recent paper dealing with the mass spectrum of elemental sulfur, Dudek and Dudek [8] discuss this spectrum in detail and also examine the octamer by MS-MS using an E-B spectrometer.

The ion trap mass spectrometer (ITMS), with its simple implementation of MS-MS [9,10] and its ability to perform chemical ionization experiments [11] recommended itself in a reexamination of the mass spectrum of sulfur. Furthermore, since collisional activation with the ion trap involves lower energies than found in sector spectrometers [9], less fragmentation than that observed by Dudek and Dudek [8] was expected.

EXPERIMENTAL

A Finnigan ion trap mass spectrometer (ITMS) was used for all measurements. Sulfur was admitted via direct insertion probe from crystalline sulfur. Reagent gases were purified grades of isobutane, methane, and ammonia (Matheson). Ions were generated and reacted (CI) under optimum ion trap conditions, i.e., with care to keep the ion/neutral content well below saturation to avoid self-CI [11-13]. Ions to be studied were trapped using a combination of ring electrode r.f. and d.c. voltages [10]. Trapped ions were then fragmented by the application of 400 mV of r.f. at the appropriate resonance frequency to the end caps of the trap for 10 ms. Daughter ions were swept from the trap by increasing the r.f. voltage on the ring electrode while applying 6 V of 530 kHz oscillation to the endcaps to enhance resolution.

RESULTS

Figure 1A shows the mass spectrum of sulfur obtained with the ITMS at 150°C in the ordinary electron impact mode. The main difference between this spectrum and one obtained using an ordinary magnetic spectrometer (LKB-9000) at 70 eV (not shown) is the lower abundance here of m/z 64 (S_2^+). However, Fig. 1A does closely resemble the spectrum of sulfur obtained by Berkowitz and Marquardt [4] who admitted the sample at 83°C from a Knudsen cell to ensure equilibrium among the various oligomers in the vapor. Other spectra reviewed in that paper reveal that the abundances of the ions S^+ and S_2^+ increase markedly with temperature. By combining previously measured vapor pressure measurements with equilibrium constants from dissociation of metal sulfides, these authors determined that sulfur vapor at 87°C consists of 69% S_8 , 7% S_7 , 25% S_6 , and 0.018% S_5 ; negligible amounts of other species are present. On the other hand, Meyer (ref. 3, p. 382), compiling data from several sources, states, "At low temperature, S_8 accounts for over 90% of the vapor, while S_6 and S_7 makes up the rest; . . ." Our data, though not obtained under equilibrium conditions (see below), also suggest a higher value for the concentration of S_8 .

In spectra where lower mass ions represent oligomers that may be plausibly derived from the parent ion either by thermal dissociation or ion fragmentation, it may be difficult to distinguish between the two processes. MS-MS

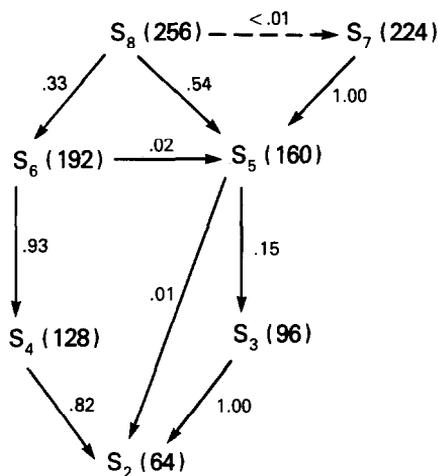


Fig. 2. Complete fragmentation scheme of S_8 obtained with the ITMS.

analysis is useful here, and the extent of fragmentation is especially easy to determine using the ITMS. Ions are collisionally activated simply by adding a supplemental a.c. voltage to the end caps. The greater velocity they acquire increases the force of their collisions with the ambient helium buffer gas [9]. For example, Fig. 1B shows the dissociation of the molecular ion of sulfur under these relatively low energy conditions. The difference between this type of collisional activation and that obtained in the higher energy realm used by magnetic spectrometers (Fig. 1C, from ref. 8) is significant: primarily S_2 and S_3 are lost in the lower energy realm; the exception being the $S_3 \rightarrow S_2$ conversion. In fact, these transitions are also the only ones detected as metastables under the higher energy conditions [8]. Ions below m/z 260 in Fig. 1C therefore result either from very fast processes occurring within the molecular ion or from secondary fragmentation of ions below S_8^{+} . Such multiple step reactions are not distinguished in one experiment with magnetic instruments.

The process of examining each ion in a complete mass spectrum can be tedious even with the ITMS. We have recently automated the process [14] and Fig. 2 depicts the complete fragmentation pattern for S_8 . A constant 400 mV was applied for 10 ms to the end caps and the efficiency of the process was $> 95\%$ in each case. Except for S_8^{+} (where loss of S_3 is important), loss of S_2 from S_7^+ , S_6^+ , S_5^+ , and S_4^+ predominates under these conditions. The ionic form of S_5 appears to be comparatively more stable. Loss of S^+ occurs only from S_8^{+} and S_3^+ . The ion S^{+} is not a product of any of these reactions, presumably due to its relatively high appearance potential of 14.0 ± 0.3 eV [4].

While the ion at m/z 256 consists of eight ^{32}S atoms, the ion at m/z 258

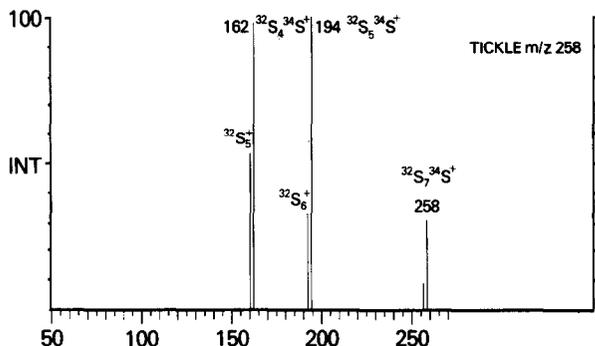


Fig. 3. MS-MS of m/z 258 ($^{32}\text{S}_7,^{34}\text{S}^+$) showing the expected isotopic combinations.

contains seven ^{32}S and one ^{34}S atoms. Loss of S_2 from the latter ion can then occur in two possible isotopic combinations: $^{32}\text{S}^{32}\text{S}$ and $^{34}\text{S}^{32}\text{S}$. Figure 3 shows that the ratio of these losses is in accord with the expected statistical result. Inspection of possible cleavages of linear and cyclic forms of S_8^+ shows that the spectra can be expected to give no information on its structure. However, the observed ratio is a good test of the mass homogeneity of the trapped ion. The small peak at m/z 256 in Fig. 3 is probably due to charge exchange between m/z 258 and the lower mass isotopomer.

Chemical ionization methods are especially easy to apply using the ion trap [11]. In fact, ion/molecule reactions occur so easily that the $(\text{M} + \text{H})^+$ ions can be something of an annoyance. Ions formed from a compound often combine with neutrals of the same substance, thus serving as their own reagents ("self-CI") [13]. This does not appear to occur with S_8^+ since no ions are seen at masses above m/z 256 even when this ion is trapped for the relatively long time of 5 ms.

Using methane as a reagent gas, the CI spectrum of S_8 shows an abundant $(\text{M} + \text{H})^+$ ion at m/z 257 (Fig. 4A). In contrast to EI, this even-electron ion loses only S_2 to give an ion at m/z 193. The masses of the other ions in the spectrum clearly reveal that the main fragmentation must be derived from the $(\text{M} + \text{C}_2\text{H}_5)^+$ adduct ion, even though this species fails to make its own appearance. Loss of S_5^+ predominates in this process, giving m/z 125. We recall that the ion corresponding to S_5^+ was also the most resistant to tickling (combined fragmentation = 0.16) at 400 mV (Fig. 2), reaffirming unusual stability for this oligomeric ion. Since the reagent ions C_2H_5^+ and CH_5^+ are present in nearly equal amounts under these conditions [11], the relative cross-sections for proton transfer and alkyl adduct ion formation with S_8 must be comparable. This contrasts strongly with most organic compounds where proton transfer predominates.

Use of isobutane as reagent gas provides only a very small peak for the

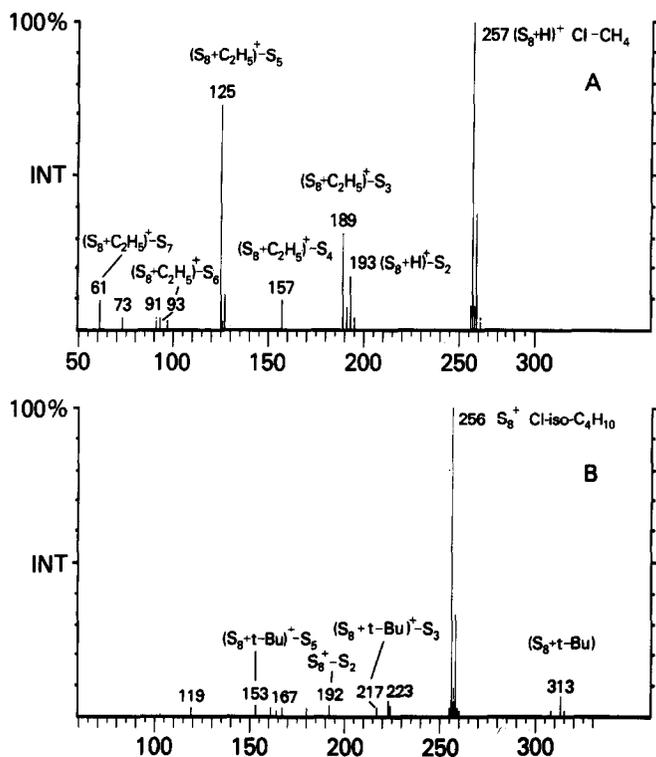


Fig. 4. Methane CI spectrum of S_8 obtained with the ITMS. (B) Isobutane CI spectrum of S_8 obtained with the ITMS.

$(M + C_4H_9)^+$ adduct ion at m/z 313 (Fig. 4B). Instead, the main process is charge exchange to give M^{++} at m/z 256. Lack of fragmentation of this ion supplies assurance that it is not formed by electron impact. Furthermore, the failure to detect any $(M + H)^+$ ions of lower oligomers suggests, in accord with Meyer's analysis [3], that the vapor is indeed mostly S_8 . On the other hand, in our experiments the sample of solid sulfur is presented to the electron beam in an open glass cup directly adjacent to the ion source. The vapor evolving from this specimen is unlikely to represent the true equilibrium concentration of all oligomers of sulfur at that temperature.

Use of ammonia (proton affinity $205 \text{ kcal mol}^{-1}$ [15]) as a reagent gas likewise provides only charge exchange with sulfur (Fig. 5A). This can hardly come about via charge exchange from NH_4^+ and more probably results from charge exchange with NH_3^+ . The possibility that the ion at m/z 256 was in fact derived from charge exchange with water that is likely to be present with the ammonia reagent gas was considered. However, a second experiment using only background water as reagent gas (proton affinity $173 \text{ kcal mol}^{-1}$ [15])

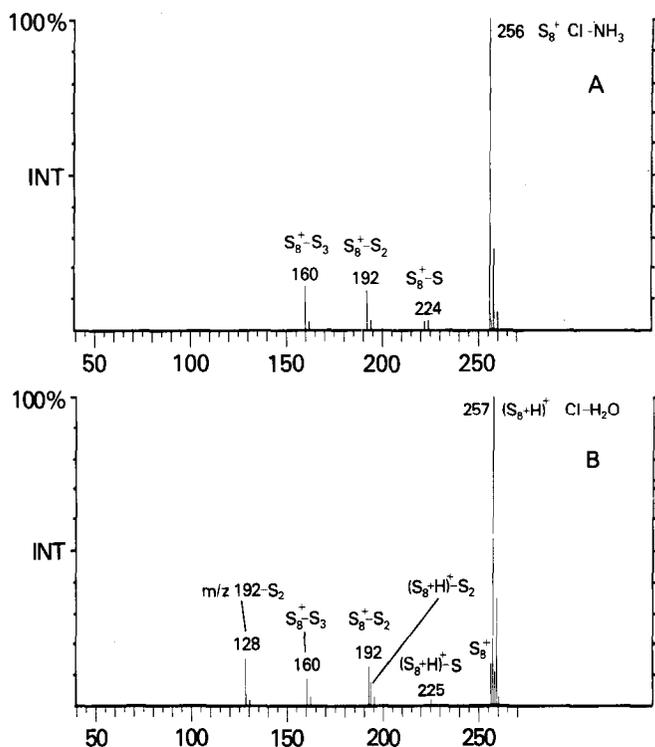


Fig. 5. Ammonia CI spectrum of S₈ obtained with the ITMS. (B) Water (air) CI spectrum of S₈ obtained with the ITMS.

showed that the H₃O⁺ ion easily transfers its proton to S₈, providing an abundant (M + H)⁺ ion at m/z 257 (Fig. 5B). Excitation of this ion (Fig. 6A) shows that it is responsible mainly for the small loss of S₂ at m/z 193, as in the case with the corresponding ion derived from methane CI. The main source of the fragment ions observed in Fig. 5B therefore must be the small amount of S₈⁺ seen in Fig. 5B that is formed by charge exchange with background ions such as N₂⁺ and H₂O⁺. Proof of this is seen in Figs. 6B and 6C where this ion and that at m/z 192 were separately isolated and tickled providing the lower mass species.

Sulfur (S₈) seems likely to be more basic than oxygen (O₂) (proton affinity 100.4 kcal mol⁻¹ [15]) but no values could be found in the literature for its proton affinity. Our data indicate this value should be about 180 kcal mol⁻¹, i.e. between water (173.0 kcal mol⁻¹ [15]) and isobutene (196.9 kcal mol⁻¹ [15]).

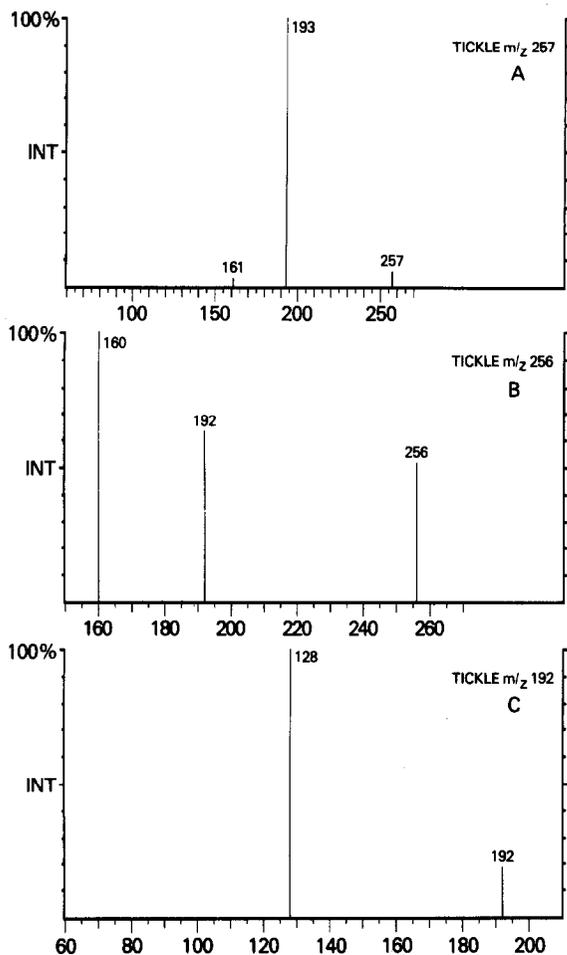


Fig. 6. MS-MS spectrum of $S_8 + H$ (m/z 257) showing loss of S_2 . (B) MS-MS spectrum of S_8^+ obtained by putative charge exchange with N_2^+ . (C) MS-MS spectrum of daughter ion m/z 192 from S_8^+ derived as in (B).

CONCLUSIONS

With the E-B geometry spectrometer, the MS-MS spectrum of a parent ion results from comparatively high energy collisions and often includes ions obtained from subsequent collisionally-induced fragmentation of daughter ions. Thus, the MS-MS spectrum of S_8 obtained in this manner resembles the normal EI spectrum (Fig. 1B). In contrast, once an ion fragments in the ITMS it is no longer in resonance at the frequency applied to its parent. Hence, it collapses to a stable orbit in the center of the trap and is no longer exposed to the excitation of the external a.c. field; thus, only single step fragmentations

tend to be detected. In the case of sulfur this provides a more detailed stepwise picture of its depolymerization than seen by use of the former technique.

While the chemical ionization experiments described here are not unique to the ITMS, the ability of this device to isolate and excite selected ions can clarify complexities due to the many events possible in such experiments.

The use of S_8 as a reagent gas in its own right, interacting with organic compounds, appears not to have been attempted. In view of the instability of the $(S_8 + C_2H_5)^+$ ion, study of its interaction with olefins might be interesting.

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