Generation and Identification of Ionic and Neutral Dithioformic Acid [HC(S)SH]•+/o, Dimercaptocarbene [HSCSH]•+/o, and Dithiirane [H2C(S2)]•+/o: a Neutralization−Reionization Mass Spectrometry and Theoretical Study[†]

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Results of tandem mass spectrometric experiments characterize both ionic and neutral dithioformic acid **a**, dimercaptocarbene **b**, and dithiirane **c** in the gas phase. Observed collisional activation spectra of the ion at *m/z* 78 from compounds ethyl carbamoylmethane dithioate **1**, 5-amino-1,3,4-thiadiazole-2-thiol **2**, and rhodanine **3** and 1,2-dithiacyclopentane **4** are most compatible with the connectivities **a**, **b**, and **c**, respectively. The NRMS experiments on these structurally characterized ions reveal that the neutral dithioformic acid **a**, dimercaptocarbene **b**, and dithiirane **c** are viable species in the gas phase. Relative energies of the CH_2S_2 isomers and their radical cations calculated at the B3LYP/6-31G** level support these experimental observations. Comparisons are made between the relative energies of the oxygen and sulfur analogues. The high relative energy of dioxirane **g** in relation to dithiirane **c** makes the former a difficult target for experimental observation.

Introduction

The neutralization−reionization mass spectrometry (NRMS) has been established as a powerful and versatile technique for investigating experimentally elusive molecules which are fundamentally important.[1−10] Using the technique of NRMS, experimental evidence has been provided for the stability of several unusual species which occur as key intermediates in organic reaction mechanisms, photochemical reactions, spectroscopic studies, and also in interstellar matter. Such species are difficult to examine by other experimental techniques, except for matrix isolation and molecular beam spectroscopy, because of their high tendency to undergo polymerization and dissociation, etc. The compounds containing −S−C(=S) groups are important intermediates in biological processes. Raman resonance probes for monitoring catalytic events within an enzyme's active site also involve dithiocarboxylic groups.[11−13] In view of this we have undertaken the study on dithioformic acid (**a**) and its isomers, viz., dimercaptocarbene (**b**) and dithiirane (**c**) which have attracted the attention of both experimentalists and theoreticians.

The dithioformic acid is also important from the viewpoint of interstellar chemistry as it has been proposed as a potential interstellar molecule.[14] It has never been isolated in the condensed phase, but its trimer was prepared by the reaction between K[HCS2] and aq HCl.[15] It was also identified by its microwave spectrum as the product in the pyrolysis of methanetrithiol.[14] Bohn et al.[16] characterized this molecule as a major product in the condensation reaction between hydrogen and CS_2

in solid argon at 12 K using matrix infrared spectroscopy. Recently Haung et al.[17] reported the unimolecular pyrolysis mechanism of dithioformic acid, and the ab initio study at SCF and MP2 levels predicted the trans dithioformic acid to be more stable than its cis isomer. Xie et al.[18] also investigated the pyrolysis of dithioformic acid using the SCF MO method at the MP4/6-31G**//HF/6-31G** level. Another important isomeric species of **a** is dimercaptocarbene **b**. Although, several carbenes, viz., H−C̈−NH2,[19] H−C̈−OH,[20] F−C̈−OH,[21] H3C−C̈−OH,[22] H2N−C̈−NH2,[23] HO−C̈−NH2, and HO−C̈−N(H)-CH3[24] have been generated and identified by NRMS, there is no report in the literature on **b**. Burgers and co-workers demonstrated by NRMS that the oxygen analogue, dihydroxycarbene (HO−C̈−OH), is a stable molecule in the gas phase.[25] Lahem et al.[26] also characterized hydroxymercaptocarbene (HS−C̈−OH) based on the observation of competitive losses of SH• and OH• from the iosmeric ethyl thioformates.[22b] The third possible isomeric species, dithiirane **c**, has also never been isolated in liquid phase, but it was proposed as a reactive intermediate in the reaction between morpholine and ClCH2−S−S−COCH3[27] and also in the photolysis of thietane in the presence of atomic sulfur.[28]

Although there are a few reports on the theoretical calculations on these species, there is no study wherein all of the species were considered at the same level of theory. All of these studies suggest that dithioformic acid is the most stable. According to MNDO and ab initio molecular orbital calculations performed at MP4/6-31G**//RHF/3-21G* level, **a** is more stable than **b** by 43.3 kcal/mol and the energy barrier for the rearrangement of **b** to **a** is 32.19 kcal/mol.[29] These authors have not considered the isomer **c** in their study. Suk Ping So also performed MO calculations on three isomers, viz., **a**, **c**, and thiosulfine (**d**) at the HF/321G* level with electron correlation at the MP2 level.[30]
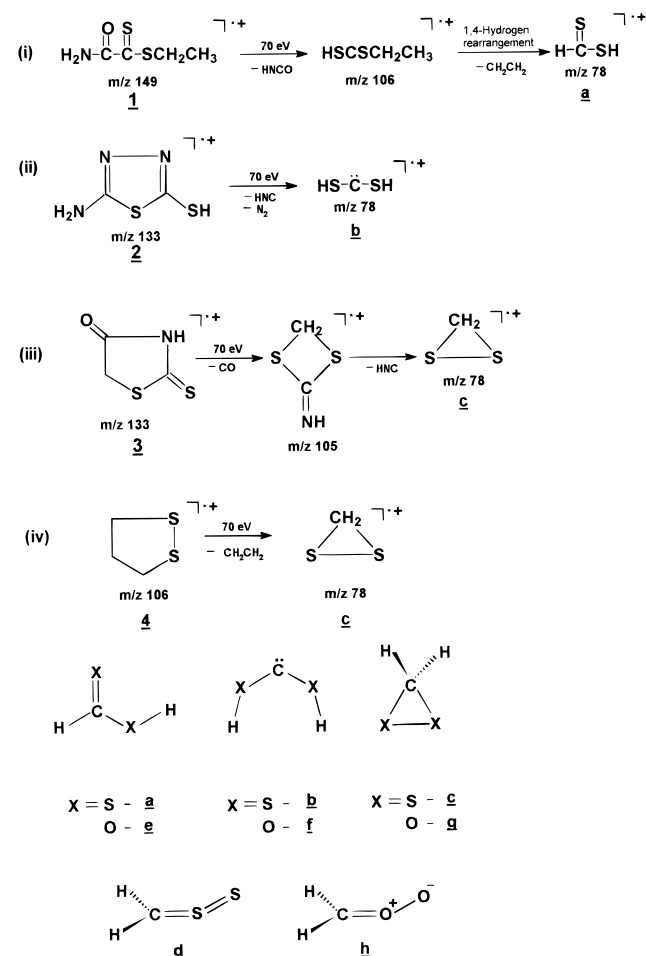

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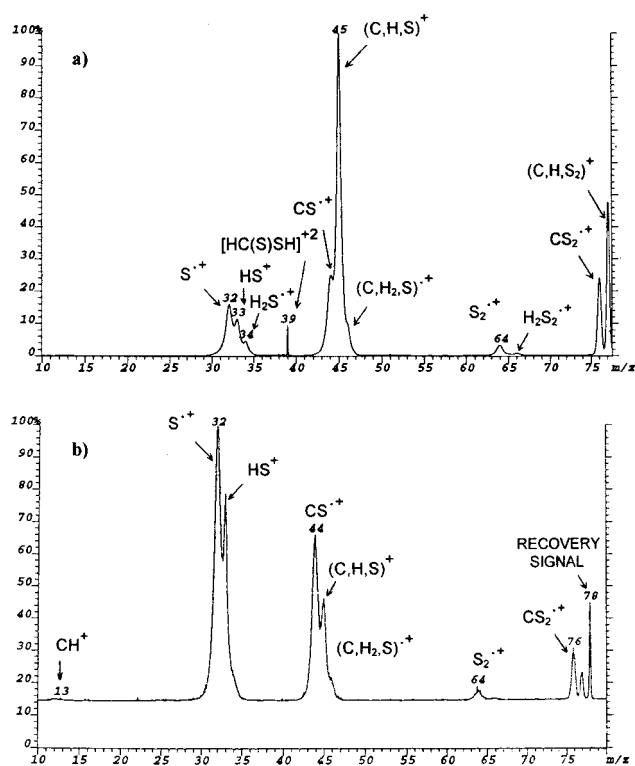[§] E-mail: jemmis@uohyd.ernet.in.

TABLE 1: Total and Relative Energies of the Isomers of CH_2S_2 and CH_2O_2 and their Radical Cations at the B3LYP/6-31G Level**

	energy (au)		relative energy (kcal/mol)	
species	neutral	radical cation	neutral	radical cation
a	−835.67098	−835.34364	0.0	0.0
b	−835.60288	−835.30834	42.7	22.2
c	−835.66074	−835.34734	6.4	−2.3
d	−835.64391	−835.31547	17.0	17.7
e	−189.76222	−189.35833	0.0	0.0
f	−189.67951	−189.35195	51.9	4.0
g	−189.61828	−189.23230	90.3	79.1
h	−189.57992	−189.22712	114.3	82.3

SCHEME 1

Figure 1. (a) CA spectrum (O_2, 80% T) and (b) NR spectrum of HC-(S)SH$^{•+}$ ($\mathbf{a}^{•+}$) ions (Xe, 80% T; O_2, 80% T) generated from **1**.

These calculations predicted that **c** is less stable than **a** by 8.24 kcal/mol. As there are no theoretical calculations on the cation radicals of **a**−**d** in the literature except one on radical cation of **a**, we have studied the energies of radical cations and neutrals of these species (**a**−**d**) at a uniform level using the B3LYP/6-31G** method.

We also compare the relative energies of the CH_2S_2 isomers with those of the corresponding CH_2O_2 species. Experimentally, formic acid (**e**) and dihydroxycarbene (**f**) have been characterized using NRMS.[25] Dioxirane (**g**) and carbonyl oxide (**h**) have eluded observation in the gas phase. Though there are several calculations reported in the literature on **g** and **h**,[31−34,43] we could not find these at the B3LYP/6-31G** level. Contrasting relative energies calculated for the oxygen and sulfur analogues point to the difficulties involved in obtaining **g** and **h** in the gas phase. We also present the generation and characterization of radical cations of **a**, **b**, and **c** using tandem mass spectrometric experiments.

Experimental

All of the mass spectrometric experiments were carried out using a VG Micromass Autospec M mass spectrometer of E_1-BE_2 geometry[35] (E denotes an electric sector and B, magnetic sector). The instrument has two collision chambers (Cls-2 and Cls-3) and an intermediate deflector electrode, all in the third field free region (between E_1B and E_2). Compounds **1** and **4** were synthesized according to procedures in the literature.[36] Compounds **2** and **3** were purchased from Aldrich and used without further purification. The samples were introduced into the ion source via the direct insertion probe under the following conditions: source temperature, 250 °C; electron energy, 70 eV; trap current, 250 μA; accelerating potential, 8 kV. High-resolution data for the ions at m/z 78 from compounds **1, 2, 3,** and **4** were obtained at a resolution of $m/\Delta m = 7000$ (10% valley definition), using the data system. Collisional activation[37] (CA) spectra were recorded by mass selecting the beam of m/z 78 ions using E_1B (MS-1), with 8 keV translational energy, and allowing collisions with oxygen in the collision cell Cls-3; the resulting ions were analyzed by scanning E_2 (MS-2). The mass analyzed ion kinetic energy (MIKE) spectra of various ions were recorded in the 3FFR by scanning E_2.

The NRMS experiments were conducted by mass selecting the beam of ions with m/z 78 with E_1B and neutralizing them in Cls-2 with xenon. The remaining ions were deflected away from the beam of neutrals by means of a deflector electrode (+5kV). The neutral beam was reionized in Cls-3 with O_2 target gas, and the resulting ions were recorded by scanning E_2. The spectra shown are accumulations of 25−50 scans.

Method of Calculation. All calculations were carried out at the B3LYP level[38] using the 6-31G** basis set[39] and GAUSSIAN 94 program.[40] The dithioformic acid (**a**), its isomers (**b, c,** and **d**), and the oxygen analogues **e, f, g,** and **h** were calculated to be minima at this level (Table 1 and Figures 7 and 8). Transition structures between the neutral species of **a** and **b**
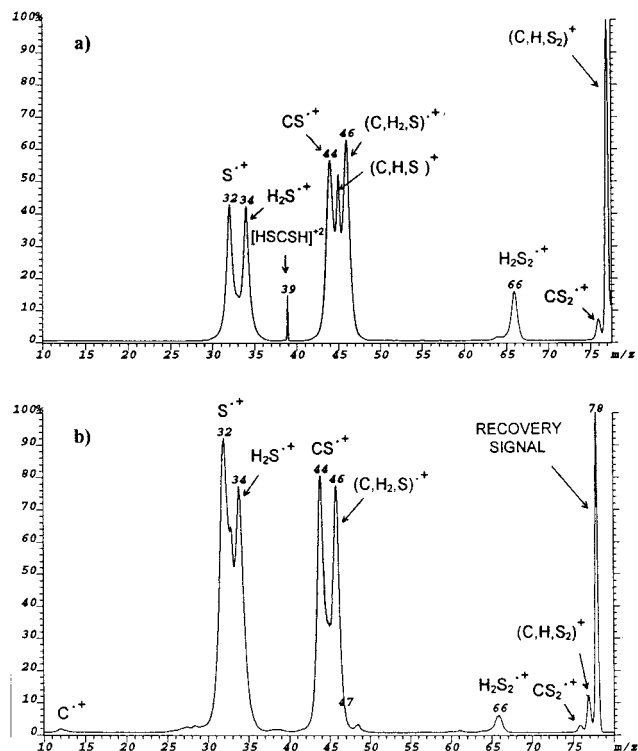
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Figure 2. (a) CA spectrum (O_2, 80% T) and (b) NR spectrum of HS−C−SH$^{•+}$ (**b**$^{•+}$) ions (Xe, 80% T; O_2, 80% T) generated from **2**. The peaks at m/z 28.5, 38.5, 48.5, and 61 of negligible intensities are artifacts.

(TS1), **a** and **c** (TS2), and **c** and **d** (TS3) were calculated to have one imaginary frequency each (Figure 6).

Results and Discussion

[C,H$_2$,S$_2$]$^{•+}$. The 70 eV electron ionization mass spectrum of ethyl carbamoylmethanedithioate (**1**) affords an abundant ion at m/z 78 (60%) whose expected elemental composition was confirmed by high-resolution experiment (measured: 77.959311; 0.5 mDa, 6.2 ppm). The linked-scan (B/E = constant) spectra of molecular ion (M$^{•+}$) and the ion at m/z 106 indicate that this ion is formed by a loss of HNCO from the M$^{•+}$ ion followed by C_2H_4 from the ion at m/z 106 (Scheme 1(i)). Four conceivable isomeric structures (**a**−**d**) can be envisaged for the ion at m/z 78. To examine the connectivity of the ion at m/z 78 its CA spectrum (Figure 1a) was studied. The major fragmentation noticed involves the loss of H$^•$ radical and SH$^•$ radical, giving rise to the ions at m/z 77 (C,H,S$_2$)$^+$ and m/z 45 (HCS$^+$/CSH$^+$), respectively. Fairly abundant peaks at m/z 33 (SH$^+$), m/z 32 (S$^{•+}$) and an intense narrow signal at m/z 39, due to a doubly charged [M]$^{+2}$ ion, are also seen in the spectrum. Weak abundance peaks at m/z 66, m/z 64, m/z 46, and m/z 34 corresponding to the $S_2H_2^{•+}$, $S_2^{•+}$, (C,H$_2$,S)$^{•+}$, and $H_2S^{•+}$ ions respectively, can be attributed to isomerization processes accompanying collisional activation. It is also known that carbon disulfide[41a] and compounds containing an −S−C(=S) group do give rise to a peak at m/z 64 ($S_2^{•+}$) in their EI and CA spectra.[41b] The structure indicative signals, viz., m/z 77 (loss of H$^•$), m/z 45 (loss of SH$^•$), m/z 33 and m/z 32 in the spectrum suggest the connectivity of dithioformic acid, HC(S)SH$^{•+}$ (**a**) for the ion at m/z 78. This view has been supported by the partial CA spectrum of m/z 78 which is shown in Figure 4a. It can be noted that this spectrum is very much similar to that of formic acid in the way that the Figure 4a shows m/z 32 (S$^{•+}$) and m/z 33 (SH$^+$) ions instead of m/z 16 (O$^{•+}$) and m/z 17 (OH$^+$).[25]
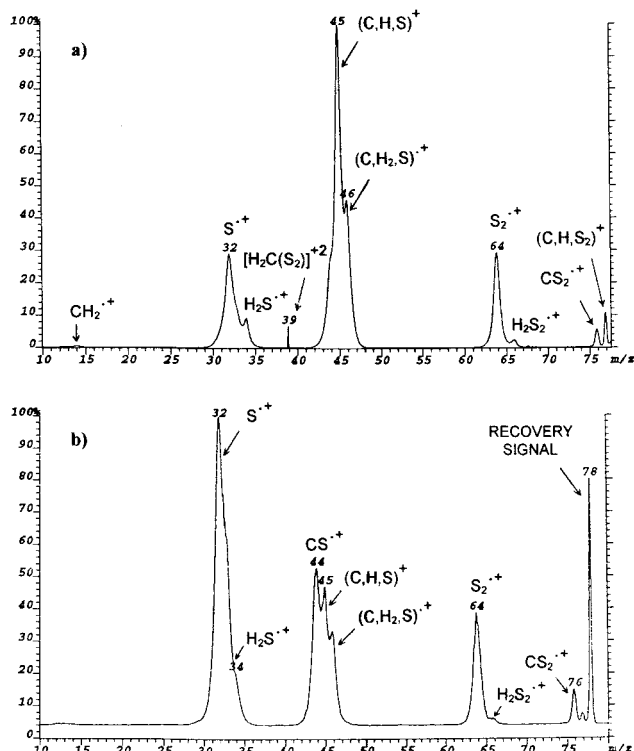

Figure 3. (a) CA spectrum (O_2, 80% T) and (b) NR spectrum of H$_2$C-(S$_2$)$^{•+}$ (**c**$^{•+}$) ions (Xe, 80% T; O_2, 80% T) generated from **3**.

Thus, on the basis of the above experimental results it can be suggested that the majority of the ions at m/z 78 from compound **1** have the structure **a**.

To investigate the stability of the neutral counterpart of HC-(S)SH$^{•+}$ ion, its NR mass spectrum was examined. The spectrum contains a fairly intense recovery signal at m/z 78 (Figure 1b) showing that the neutral HC(S)SH generated by vertical neutralization is a stable species on the NR time scale (about 0.5 μs). Further, it can be seen that all the ions that are present in the CA spectrum (Figure 1a) also occur in the NR spectrum (Figure 1b), except the charge stripping peak at m/z 39. However, there are some significant differences between the CA and NR mass spectra with respect to fragment ion abundances. The NR spectrum shows more abundant ions at m/z 45, m/z 44, m/z 33, and m/z 32. The increased abundance of these ions can be ascribed to a partial CA of neutral HC-(S)SH to form neutral fragments which undergo reionization and contribute significantly to the NR mass spectrum.

The 70 eV EI mass spectrum of 5-amino-1,3,4-thiadiazole-2-thiol (**2**) affords a weak abundance peak at m/z 78 (2%) corresponding to the [C,H$_2$,S$_2$]$^{•+}$ ion. The accurate mass measured (77.959455; 0.3 mDa, 4.3 ppm) for this ion confirms its elemental composition. As evidenced by linked-scan spectra of M$^{•+}$ ion and the ion at m/z 106, loss of HNC followed by N_2 elimination can account for the formation of the ion at m/z 78 (Scheme 1(ii)).

The CA spectrum of the ion at m/z 78 generated from **2** is found to be distinctly different from that of **1** (Figure 2a). The spectrum displays abundant ions at m/z 77 (C,H,S$_2$)$^+$, m/z 76 (CS$_2^{•+}$), m/z 46 (C,H$_2$,S)$^{•+}$, m/z 45 (CSH$^+$), m/z 44 (CS$^{•+}$), m/z 34 (H$_2$S$^{•+}$), and m/z 32 (S$^{•+}$) formed by the losses of H$^•$, H$_2$, S, SH$^•$, H$_2$S, CS, and (C,H$_2$,S), respectively. A fairly abundant diagnostic ion at m/z 66 corresponding to the loss of a C atom which is absent in the former CA spectrum of **a**$^{•+}$ (Figure 1a) prompts us to suggest the connectivity, the dimercaptocarbene, HSCSH$^{•+}$ ion for the peak at m/z 78 from **2**. The formation of
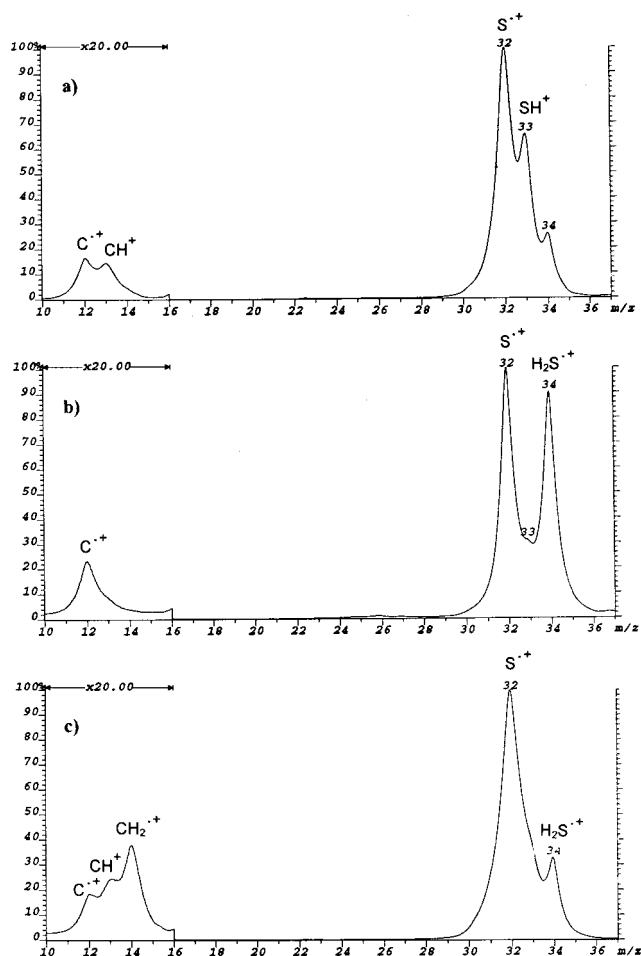
Figure 4. Partial CA spectra (a) HC(S)SH[•+] (**a**[•+]), (b) HSCSH[•+] (**b**[•+]), and (c) $H_2C(S_2)$[•+] (**c**[•+]) ions generated from **1**, **2**, and **3**, respectively.

Figure 5. (a) CA spectrum (O_2, 80% T) and (b) NR spectrum of H_2C-(S_2)[•+] (**c**[•+]) ions (Xe, 80% T; O_2, 80% T) generated from **4**.

H_2S_2[•+] ion is in contrast to the oxygen analogue where the corresponding H_2O_2[•+] ion was absent.[25] This may be attributed to more diffuse orbitals of S which trigger the S—S bond formation. This assignment is further supported by the partial CA spectrum (Figure 4b) of the ion at m/z 78, which is again similar to that of dihydroxy carbene HOCOH[•+] ion in the way that this spectrum show S[+•] and H_2S[•+] instead O[•+] and H_2O[•+] ions.[25] A charge stripping peak corresponding to a doubly charged [M][+2] ion is also conspicuous in the CA spectrum. The NR mass spectrum of HSCSH[•+] ion (Figure 2b) showing an abundant recovery signal and all the tell-tale peaks strongly suggests that the neutral dimercaptocarbene is a viable molecule in the rarefied gas phase.

The molecular ion of rhodanine **3** loses a molecule of CO followed by HNC (Scheme 1(iii)) to afford an ion at m/z 78 (3%) whose elemental composition has been confirmed by high-resolution technique (77.959707; 0.1 mDa, 1.1 ppm). Interestingly, the CA spectrum of the ion at m/z 78 (Figure 3a) generated from **3** is found to be different from those of **1** and **2** (Figures 1a and 2a). The major differences are caused by the abundant ions at m/z 64 (S_2[•+]) formed by loss of CH_2 carbene and the characteristic ions at m/z 14 (CH_2[•+]) in addition to the ions at m/z 13 (CH[+]) and m/z 12 (C[•+]) as shown in the partial CA spectrum (Figure 4c). This structure-indicative group suggests that the majority of the ions of m/z 78 from compound **3** seem to be formed with the connectivity of either dithiirane (**c**[•+]) or thiosulfine (**d**[•+]). On the basis of the theoretical caculations,[30,42] which predict that ionic and neutral **c** are thermodynamically more favorable than **d** by 20 and 10.6 kcal/mol respectively,
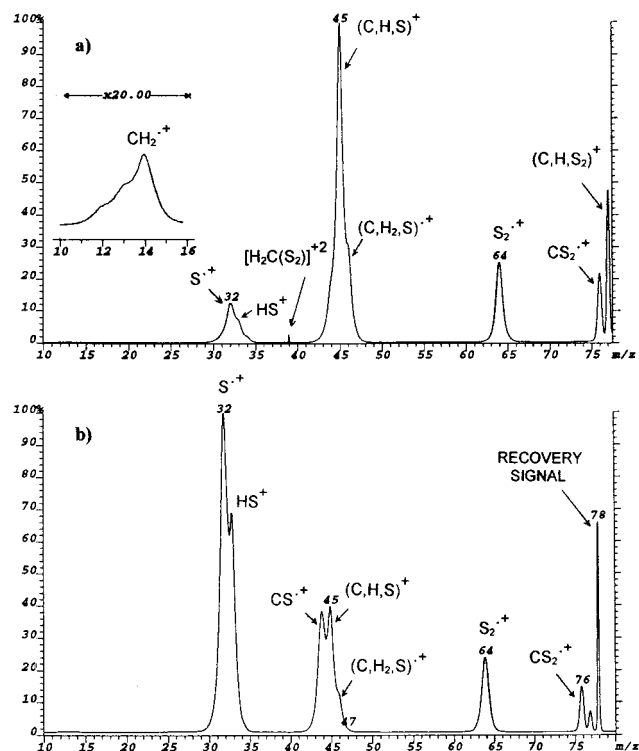
the predominant formation of **d** can be ruled out. The NR mass spectrum of this ion is given in Figure 3b. The spectrum displays intense survivor ion and all fragment ions that are seen in the CA spectrum (Figure 3a), predicting that the neutral dithiirane (**c**) is a stable species on the NR time scale.

A possible precursor for generating thiosulfine (**d**[•+]) is 1,2-dithiacyclopentane[36b,44] (**4**). The EI spectrum of **4** shows a fairly abundant signal at m/z 78 (23%) corresponding to the $[C,H_2,S_2]$[•+] ion. The elemental composition of this ion has been confirmed by accurate mass measurement (measured: 77.959671; 0.1 mDa, 1.6 ppm). This ion can be formed by the loss of C_2H_4 from the M[•+] ion of compound **4** which has been supported by its MI spectrum ([Scheme 1(iv)]). Surprisingly, the CA and NR spectra (Figure 5) of m/z 78 were found to be similar to those of **c**[•+] except for a small difference. The peak at m/z 66 (H_2S_2[•+]) is virtually absent in these spectra. On the basis of these results, it can be suggested that the ion with m/z 78 formed from compound **4** corresponds to a relatively "purer" dithiirane species as compared to the **c** generated from compound **3**.

The relative energies calculated for neutrals and radical cations of **a**−**c**[•+/o] at B3LYP/6-31G** level (Table 1) agree with experimental observations and with our assignment of the structures. They also reveal that all the three species, **a**−**c**[•+/o] lie on CH_2S_2 potential energy surface and do not undergo easy isomerization because of the high energy barrier between them (Figure 6). The conversion of **a** to **b** involves the TS1 with a barrier of 74.0 kcal/mol. The barrier is somewhat lower for **a** to **c** (TS2, 55.7 kcal/mol). The lowest barrier calculated for the conversion of **c** to **d** is still substantial (TS3, 36.0 kcal/mol). Thermodynamically, **c** is more stable than **d** by 10.6 kcal/mol. The full set of optimized equilibrium structures for the neutrals and radical cations of HC(S)SH **a**, HSC̈SH **b**, $H_2C(S_2)$ **c**, and H_2CSS **d** are given in Figure 7. Thiosulfine (**d**) is more favorable than dimercaptocarbene (**b**) by 25.7 kcal/mol. The corresponding oxygen analogues (formic acid **e**, dihydroxycarbene **f**, dioxirane **g**, and carbonyl oxide **h**) are shown in Figure 8. The three-
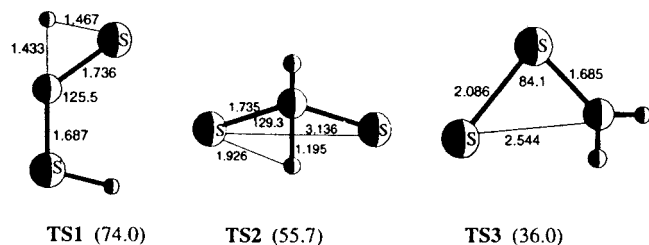
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TS1 (74.0) **TS2** (55.7) **TS3** (36.0)

Figure 6. Structures and relative energies (kcal/mol in parenthesis) of the transition structures (TS1 between **a** and **b**, TS2 between **a** and **c**, and TS3 between **c** and **d**) at the B3LYP/6-31G** level for CH_2S_2 isomers.
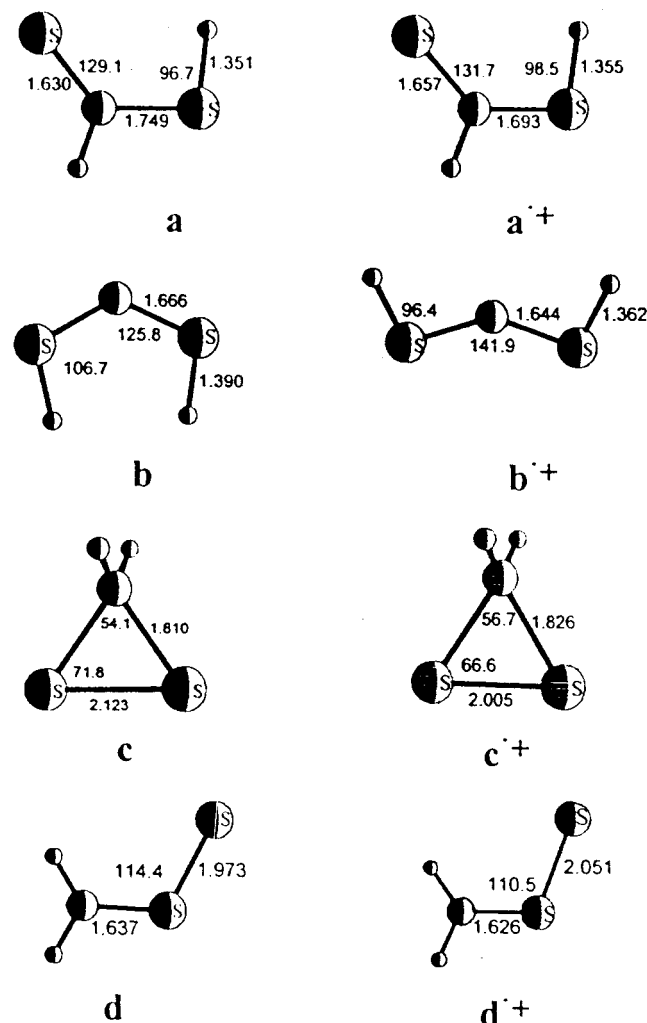

Figure 7. Calculated geometries of the neutral CH_2S_2 isomers and their radical cations at the B3LYP/6-31G** level.

membered dithiirane (**c**) is indeed quite low in energy in relation to that of the oxygen analogue **g**. The dioxirane (**g**) is found to be 90.3 kcal/mol higher in energy than **e**. However, the relative energy of dihydroxycarbene **f** is comparable to that of the dithio analogue **b**. The unusually high energies of **g** (90.3 kcal/mol) and **h** (114.3 kcal/mol) relative to **e** make them difficult targets to be observed in the gas phase. Our calculated energy difference agrees well with the detailed studies on dioxirane and dicarbonyloxide reported earlier.[43] We calculate the radical cations of **g** and **h** also to be very high in energy (Table 1).

The decrease in the relative energy of radical cations **b** and **f** arising from dimercaptocarbene (**b**) and dihydroxycarbene (**f**) is unusually large in relation to the other isomers. Perhaps the high energy of the allyl anion type orbital from where an
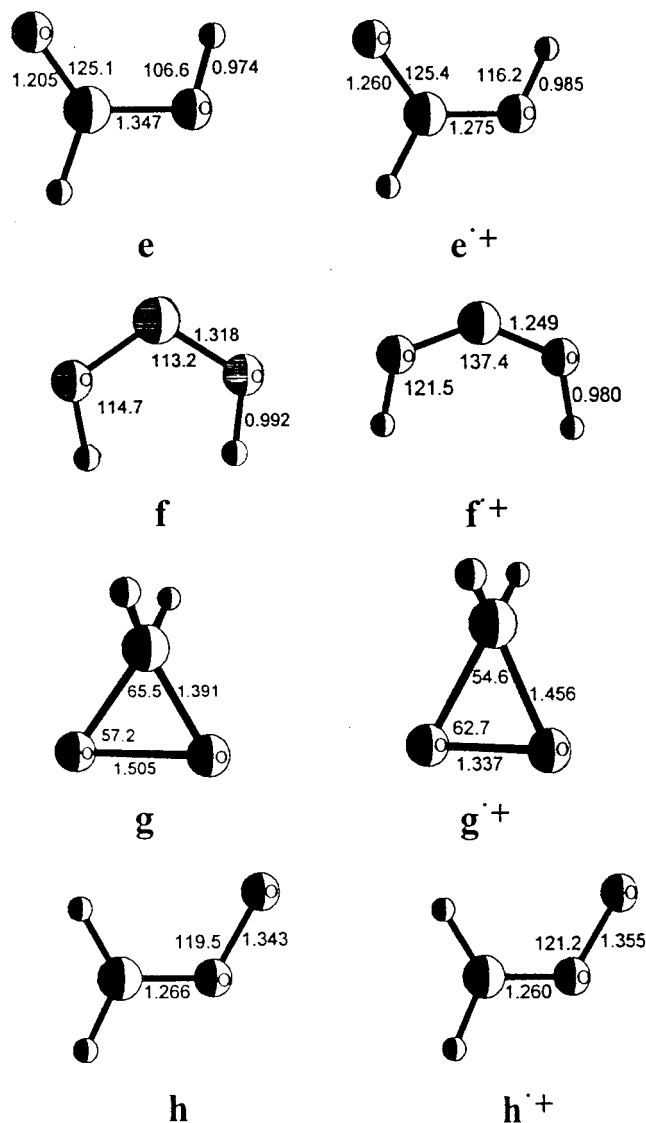

Figure 8. Calculated geometries of the neutral CH_2O_2 isomers and their radical cations at the B3LYP/6-31G** level.

electron is lost in the formation of the radical cation explains the unusual decrease in energy on ionization.

Conclusion

Collision activation experiments have established the connectivities of dithioformic acid **a**, dimercaptocarbene **b**, and dithiirane **c** for the ion at *m/z* 78 generated by electron ionization of ethyl carbamoylmethanedithioate, 5-amino-1,3,4-thiadiazole-2-thiol, and rhodanine and 1,2-dithiacyclopentane, respectively. Neutralization−reionization experiments have provided the evidence for the existence of corresponding neutral molecules HC(S)SH, HSC̈SH, and $H_2C(S_2)$ in the rarefied gas phase. The theoretical calculations on these species indicate that substantial barriers exist for the interconversion of the CH_2S_2 isomers (**a**−**d**). The contrasting relative energies of CH_2S_2 and CH_2O_2 isomers is also in tune with the difficulty in generating **g** and **h**.

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1,2-dithiacyclopentane. The work at University of Hyderabad is supported by research grants from the Department of Science and Technology and Council of Scientific and Industrial Research, New Delhi.

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