Photoelectron Spectroscopic Study of the Thermal Decomposition of 2-Pyrrolidinone and 2-Pyrrolidinethione

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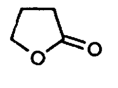
The thermal decomposition of 2-pyrrolidinone and 2-pyrrolidinethione was investigated in a flow system by following the changes in their UV photoelectron spectra at various temperatures. At *ca.* 850 °C 2-pyrrolidinone begins to decompose by a decarbonylation process into carbon monoxide, ethene, hydrogen cyanide and molecular hydrogen. By contrast, at *ca.* 800 °C, 2-pyrrolidinethione decomposes mainly into pyrrole and hydrogen sulfide. MO calculations at the PM3 and 6-31G levels provide theoretical support for the mechanisms proposed for these decompositions.

As part of our study on the reactivity of small and medium heterocyclic molecules, we have recently investigated the thermal decomposition of γ-butyrolactone **1** and γ-thiobutyrolactone **2** experimentally[1] as well as theoretically.[2] It was found that for these lactones decarboxylation and decarbonylation were the important reactions. For **1**, decarboxylation was the major reaction, while for **2** decarbonylation was the major process and loss of COS was relatively minor, as COS is a poorer leaving group than CO_2. Calculations on the potential energy profiles showed that decarbonylation proceeds in a concerted fashion while decarboxylation takes place *via* a stepwise mechanism.[2] We now extend the range of compounds studied to include 2-pyrrolidinone **3** and 2-pyrrolidinethione **4**.



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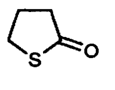

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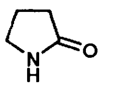

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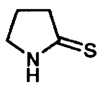

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We hope to investigate the variation in reactivity as a result of the change in electronic structure in the series. In particular, the change in atomic radius, electronegativity and polarizability in going from an oxygen to a sulfur atom have often resulted in differences in chemical behaviour between carbonyl and thiocarbonyl compounds,[3] and it is interesting to compare the decomposition pathways open to **3** and **4**.

Photoelectron spectroscopy as an analytical technique offers, among other capabilities, the advantages of small sample size and the possibility of detection of transient species,[4] two features which were important in the present work.

Experimental

Photoelectron (PE) spectra were measured on a Leybold–Heraeus UPG 200 spectrometer with resolution in the range of 18–25 meV, using argon and iodomethane as calibrant gases.

Compound **3** was obtained commercially and purified by distillation under reduced pressure. Compound **4** was prepared by the method reported in the literature.[5,6] The white solid **4** was recrystallized from xylene and had mp 112–113 °C.

As **3** was an involatile liquid and **4** was a solid, their PE spectra were recorded by using a solid sample probe, through which the sample could be vapourized near the heated ionization chamber of the spectrometer.

Pyrolysis was carried out in a flow system at low pressure. The pyrolyser consisted of a quartz tube which was 45 cm long and 1.2 cm in inner diameter and lightly packed with quartz wool. Heating was achieved through a tube oven 30 cm in length. One end of the quartz tubing was connected to the inlet system of the spectrometer. The pure compound was vapourized by heating under reduced pressure and the vapour, maintained at about 100 °C, was introduced into the heated zone through the pumping system of the spectrometer. Progress of reaction was monitored by on-line recording of photoelectron spectra of the gaseous products formed. The spectrum of either **3** or **4** was not recorded during pyrolysis because of condensation of the vapour on the walls.

A liquid nitrogen cold trap placed downstream from the heated zone was sometimes employed to collect the condensables. To measure the spectra of the individual products, the components in the trapped mixture were released through differential vapourization, by using a cold bath of liquid N_2–EtOH mixture.

Computational Details.—Calculations were performed using the PM3 Hamiltonian using a CAChe worksystem, and using the Gaussian 92 program on a Silicon Graphics workstation. Transition states were located using the eigenvector following method and shown to have only one negative force constant in the Hessian matrix.

Results and Discussion

The spectra of **3** and **4** obtained by us are shown in Figs. 1(*a*) and 4(*a*) respectively. They are in good agreement with other reported spectra.[7] As mentioned earlier, due to condensation problems, the spectra of these precursors were not recorded during pyrolysis.

Heating of **3** up to 800 °C in the flow tube did not result in any detectable changes. At 850 °C, bands at 10.5, 13.60 and 14.02 eV emerged and they became more intense at higher temperatures. A typical spectrum is shown in Fig. 1(*b*). From their ionization potentials and characteristic structures, the bands could be readily attributed to the generation of ethene, hydrogen cyanide and carbon monoxide. Heating up to 1050 °C did not give rise to further qualitative changes.

The spectrum shown in Fig. 2 was taken upon heating **3** to 950 °C, with the condensable products removed by a liquid nitrogen cold trap. The expanded spectrum shows a band at 15.9 eV. From the associated vibrational progression a frequency of *ca.* 2100 cm^{-1} could be seen. These features agreed well with those expected for molecular hydrogen.[8]

The results show that the decomposition of **3** gives rise to the formation of CO, C_2H_4, HCN and H_2 as shown in Scheme 1.

This is analogous to the decarbonylation reaction observed for **1** and **2**, where apart from the common products CO and

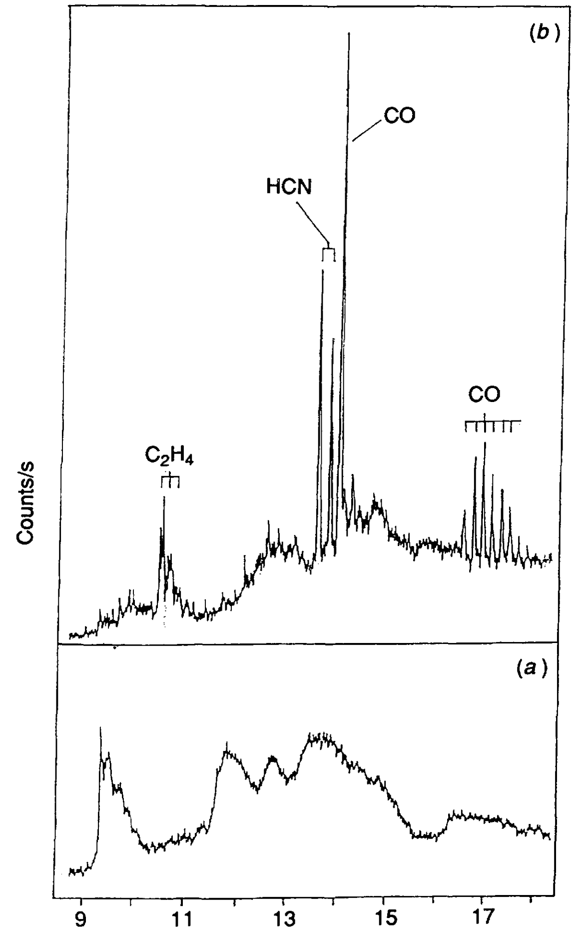
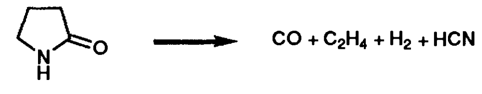
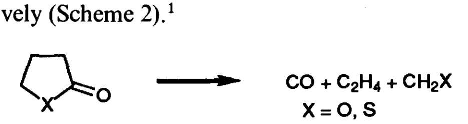


Fig. 1 (*a*) Photoelectron spectrum of **3**; (*b*) composite spectrum of products obtained upon heating **3** at 950 °C



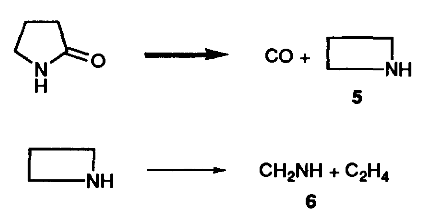
Scheme 1

C_2H_4, formaldehyde and thioformaldehyde were formed respectively (Scheme 2).[1]



Scheme 2

One possible pathway of Scheme 1 is through the formation of azetidine **5**, which under the experimental conditions would decompose to form ethene and methylenimine **6** (Scheme 3).[9]



Scheme 3

Compound **6**, in turn, would decompose to give HCN and H_2.[10]

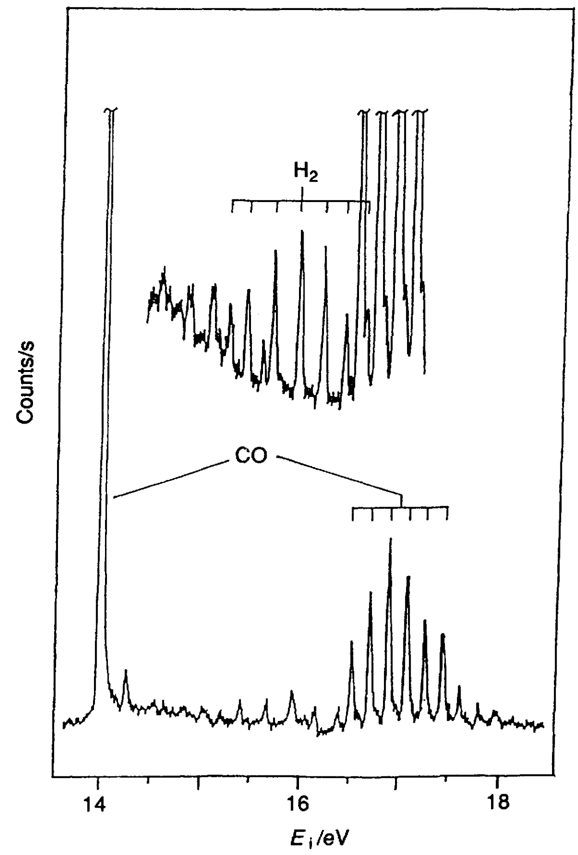


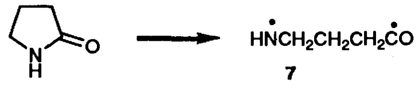
Fig. 2 Spectrum taken upon heating **3** at 950 °C, with condensable products removed with a liquid N_2 cold trap

$$\underset{\mathbf{6}}{CH_2NH} \longrightarrow HCN + H_2$$

Scheme 4

To test the importance of the intermediacy of **5** and **6** in the decomposition of **3**, the pyrolysis of **5** was carried out under the same experimental conditions. It was found that **5** started to decompose at 600 °C. At 800 °C decomposition was virtually complete and the composite product spectrum showed the presence of **6**, ethene and HCN. Figs. 3(*a*) and 3(*b*) show the spectral changes. Through differential vapourization of the trapped product sample, the spectrum of pure **6** was recorded as shown in Fig. 3(*c*), which compares closely with the spectrum reported in the literature.[10,11] Heating of **5** to 900 °C gave a spectrum similar to that shown in Fig. 3(*b*). Thus while **5** decomposed completely, **6** was relatively stable at these temperatures. Since **6** was not detected in the pyrolysis of **3**, it seems unlikely that the decomposition of **3** would proceed according to the sequence of reactions (Scheme 3).

Two other possible pathways for the decarbonylation of **3** would be through cleavage of the carbonyl C–N bond, followed by the fragmentation of the biradical intermediate species **7** (Scheme 5).



$$\underset{\mathbf{7}}{H\dot{N}CH_2CH_2CH_2\dot{C}O} \longrightarrow CH_2NH + C_2H_4 + CO$$

Scheme 5

Alternatively, decarbonylation may proceed through the following concerted process, a cycloreversion reaction (Scheme 6).

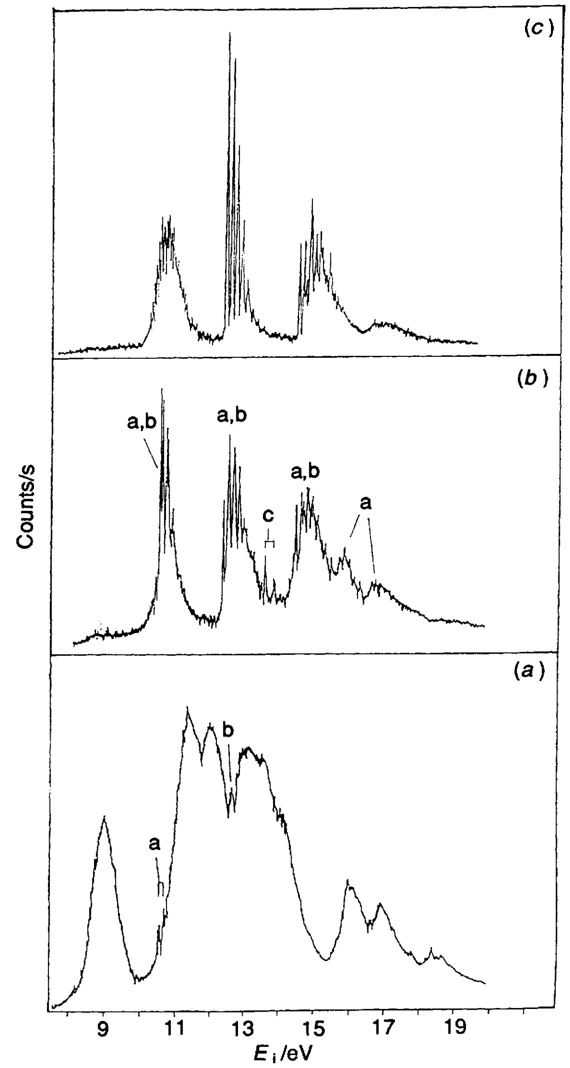
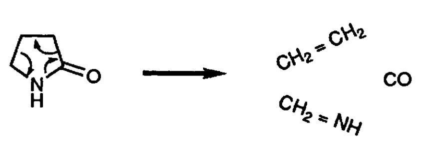


Fig. 3 Spectral changes upon heating of **5** at (*a*) 600 °C; (*b*) 800 °C. (*c*) Spectrum of **6**. Throughout: **a**, **6**; **b**, ethene; **c**, HCN. Apart from the small peaks due to **6** and ethene, the spectrum in (*a*) is that of **5**.



Scheme 6

Our experimental results show that chemical activation is probably involved in the generation of **6**, as it readily decomposes into HCN and H_2 at temperatures where it was observed, in isolation, to be stable.

Upon heating of **4**, commencement of decomposition occurred at 750 °C, when a small signal at 10.48 eV due to hydrogen sulfide could be detected. At 800 °C the presence of pyrrole as another product was revealed by its characteristic bands at 8.22, 9.22, 12.9, 13.8 and 15 eV,[12] as shown in Fig. 4(*b*). At temperatures from 750 to 900 °C, the main products were pyrrole and hydrogen sulfide. Small quantities of secondary products, not observed in the composite spectrum, could be identified through differential vapourization of the trapped mixture. These included carbon disulfide, ethene, ethyne and hydrogen cyanide. Thus it appears that the decomposition of **4** gives rise to formation of pyrrole and H_2S as the main process (Scheme 7).

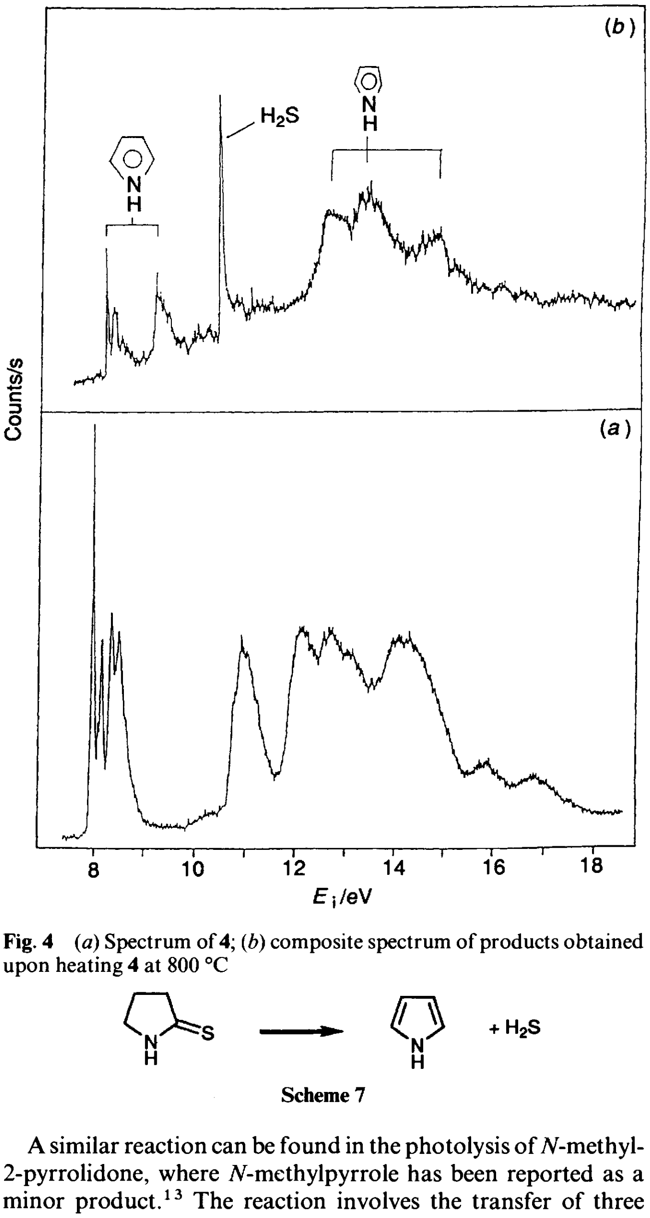
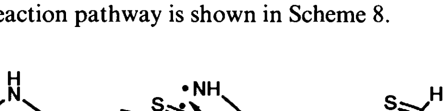
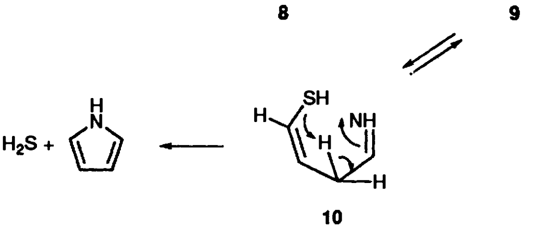


Fig. 4 (*a*) Spectrum of **4**; (*b*) composite spectrum of products obtained upon heating **4** at 800 °C



Scheme 7

A similar reaction can be found in the photolysis of *N*-methyl-2-pyrrolidone, where *N*-methylpyrrole has been reported as a minor product.[13] The reaction involves the transfer of three hydrogen atoms. Under low pressure reaction conditions, hydrogen transfer most probably is intramolecular, and a possible reaction pathway is shown in Scheme 8.



Scheme 8

The slow step in the Scheme would be the cleavage of the C–N bond in **4** with formation of the biradical **8**, since the energy barrier, which is approximately the bond dissociation energy, is expected to be the highest among the steps. This is followed by three hydrogen transfer steps leading to the final products. One of the hydrogen transfer steps proceeds through a keto–enol

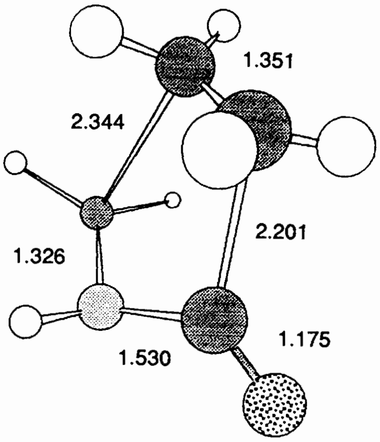


Fig. 5 Transition state of 2-pyrrolidinone **3**

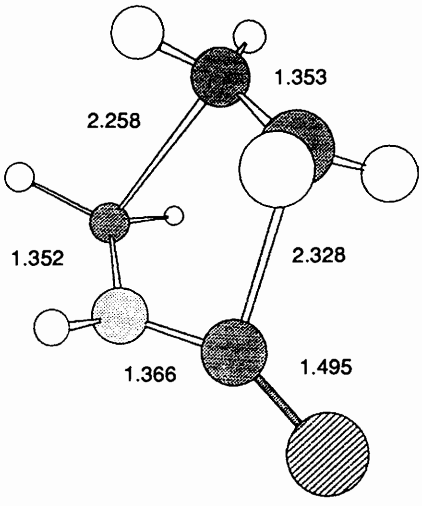


Fig. 6 Transition state of 2-pyrrolidinethione **4**

conversion in which the enethiol is expected to be the favoured tautomer.[3]

Analogous examples for the formation of **9** can be found in the photolysis of cyclopentanone[14] and **1**,[15] where pentenal and succinaldehyde are formed respectively among other products. In the thermal decomposition of **1**, as mentioned earlier, loss of CO and CO_2 were the main reactions and succinaldehyde was not detected. For **4**, the reactions analogous to decarbonylation and decarboxylation were apparently unfavourable.

Mechanistic Information from MO Calculations.—The activation energies for the C=O and C=S systems are 84.9 and 93.2 kcal mol^{-1} respectively at the semi-empirical PM3 level, thus confirming that the sulfur system has a rather higher barrier. More interesting are the transition state structures (Figs. 5 and 6 for the C=O and C=S systems respectively). For the C=O system, it clearly corresponds to the formation of ethene, $H_2C{=}NH$ and C=O. In particular, the PM3 calculated N • • • C bond length of 1.53 Å shows no double bond character and the vibrational analysis shows this bond to be cleaving in the transition state. The corresponding bond length at the *ab initio* RHF 6-31G level ($E_{total} = -284.5658$ Hartree) was somewhat longer at 1.83 Å, which clearly shows that at this level of theory, the bond is clearly cleaving. In the C=S system, the equivalent bond lengths are 1.366 (PM3) or 1.409 Å (6-31G, $E_{total} = -607.194\,39$ Hartree) which indicate a bond clearly not breaking in the transition state. Thus the primary product for the C=S system is predicted to be $H_2C{=}\overset{-}{N}H{-}\overset{+}{C}{=}S$ (a dipolar species) rather than $H_2C{=}NH$ and C=S.

Conclusion

In conclusion, substitution of the carbonyl group in **3** by the thiocarbonyl group appears to have profound effects on the decomposition pathways of the compounds and the stability of the thiocarbonyl and enethiol species relative to their oxygen counterparts seems to play an important role. Thus decomposition of **3** led to CO loss as the carbonyl form is stable, while decomposition of **4** gave rise to formation of H_2S and pyrrole; here the enethiol as a probable intermediate species is favoured by virtue of the poor p_π–p_π overlap in the thiocarbonyl group and hydrogen transfer is the preferred pathway.

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