

## Reactions of Thiophene and Alkylthiophenes in Glow Discharge \*

JAN SKRAMSTAD, MOHAMMED SHOAB CHAUDHRY and ARNE GARVANG

Institute of Chemistry, University of Oslo, P.O.B. 1033 Blindern, N-0315 Oslo 3, Norway

The glow discharge reaction of thiophene is shown to produce thioketene and carbon monosulfide along with other gaseous products. The dominant liquid product is ethynylthiophene. Methylthiophenes and especially dimethylthiophenes produce benzene as one of the major liquid products.

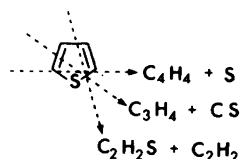
The glow discharge reaction of thiophene has been reported by Undheim.<sup>3</sup> He found polymeric material to be the major solid product and claimed sulfur, hydrogen sulfide and carbon monosulfide to be the only volatile products. In connection with a study of selected sulfur compounds in glow discharge, we had occasion to repeat this reaction and report here our results with thiophene,<sup>4</sup> methylthiophenes<sup>5</sup> and dimethylthiophenes.<sup>5</sup>

### RESULTS AND DISCUSSION

The volatile products from the glow discharge reactions of thiophene were analyzed mass spectrometrically (see Experimental). The results indicated the presence of species with molecular formulas  $C_2H_2S$ ,  $C_4H_4$ ,  $CS$ ,  $C_3H_4$  and  $C_2H_2$ . These molecules could have been formed by fragmentation/rearrangement of the thiophene ring as depicted in Scheme 1.

Here we would like to focus attention on carbon monosulfide and the structure of the  $C_2H_2S$ -species. We found it likely that the latter might be thioketene as it has been calculated<sup>6</sup> to be the preferred structure among its isomers and is reported to be stable at  $-80^\circ C$ .<sup>7</sup>

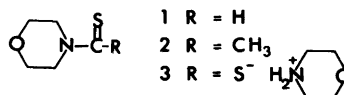
We decided to prove the presence of these reactive species by a trapping experiment with morpholine. Thiophene was passed through the



Scheme 1. Fragmentation of thiophene in a glow discharge.

plasma zone and morpholine was introduced into the cooling trap (at  $-196^\circ C$ ) after the plasma had been switched off. A GLC/MS analysis showed the presence of two thioamides: 4-thioformylmorpholine (1) and 4-thioacetylmorpholine (2), both were also identified by comparing retention times and mass spectrometrical fragmentation with authentic samples prepared according to literature.<sup>8,9</sup> In addition a white solid was present in the cooling trap. This compound did not pass through the gas chromatograph. It was identified (MS) as morpholinium morpholine-4-carbodithioate (3) by comparison with an authentic sample.<sup>10</sup>

The formation of the morpholine derivatives 1 and 2 unambiguously demonstrates the presence of  $CS$  and  $CH_2=C=S$  in the product mixture. The formation of 3 could be the result of a reaction between  $CS_2$  and morpholine or (less likely) a reaction between sulfur and either of the thioamides 1 or 2. These morpholine derivatives were also reported by Undheim,<sup>3</sup> but he considered the major route to these compounds to be the result of a reaction between sulfur radicals on a primarily formed adduct of morpholine and an



\* Part 1: see Ref. 1.

aldehyde produced by the glow discharge decomposition of morpholine. This route is of course not open in our case as the morpholine is introduced after the glow discharge has been switched off.

Carbon monosulfide has previously been generated from carbon disulfide both by pyrolysis,<sup>11</sup> electrical discharge<sup>12</sup> and photolysis.<sup>13</sup> It is known to have a singlet ground state and is observed to persist at low temperatures for times ranging from a few s to many min.<sup>14</sup> It is also present in interstellar space.<sup>15</sup> However, the chemistry of CS in solution is virtually unknown. Therefore the above-mentioned reaction between morpholine and carbon monosulfide producing the thioamide *1* is one of the first examples of its reaction with organic substrates. We plan to carry out further reactions with plasma generated CS.

When all gaseous products were evaporated from the cooling trap, the remaining liquid was analyzed by GLC/MS. The major product, amounting to almost 50 % when unreacted thiophene was excluded, was ethynylthiophene (consisting probably both of the 2- and the 3-isomer). The formation of this species appears to be the result of an attack on thiophene of an ethynyl radical produced by fragmentation of

thiophene. A similar reaction was observed when 2-phenylthiophene was treated with acetylene in a glow discharge reaction.<sup>1</sup> The remaining liquid products were: ethynylbenzene (15 %), benzothiophene (11 %), naphthalene (5 %), indene (4 %), ethylbenzene (2 %) and others (15 %).

In order to throw more light on the reactions of thiophenes under glow discharge conditions, the two methyl- and the four dimethylthiophenes were investigated. The results from the analyses of the liquid portion of the products are given in Table 1. As can be seen from the table, all six compounds give appreciable amounts (20–30 %) of unidentified products. Most of these are polyalkylated thiophenes and benzenes as judged from their GLC/MS data. Due to lack of reference compounds their identities have not been established. A product with a shorter retention time than that of benzene (compound *a* in the table) is present in all reaction mixtures. GLC/MS analysis makes it highly probable that this is identical with 2-hexen-4-yne. The formation of this compound is analogous to the formation of 4-phenyl-1-buten-3-yne from 2-phenylthiophene as reported previously.<sup>1</sup>

A striking feature of the results presented in Table 1 is the formation of benzene. Especially the dimethylthiophenes give high yields

**Table 1.** Liquid products from the reaction of methyl- and dimethylthiophenes in a glow discharge. The amount of liquid products represents about 50 % of the total yield, the rest being gaseous (30–40 %) and polymeric products (10–20 %). Of the liquid products unchanged starting material constitutes the major part (up to 50 %), but this has been subtracted from the figures in the table.<sup>a</sup>

Products	Starting materials (%)					
	2-Me	3-Me	2,3-Di-Me	3,4-Di-Me	2,5-Di-Me	2,4-Di-Me
a. 2-hexen-4-yne?	7.4	11.0	3.6	3.2	3.6	4.9
Benzene	8.6	7.7	24.7	17.6	36.9	18.2
Thiophene	15.3	13.6	3.1	1.9	2.0	1.4
Toluene	1.2	2.5	4.1	2.4	2.6	4.9
2-Me-thiophene	—	14.4	6.6	1.4	15.4	6.6
3-Me-thiophene	9.2	—	12.8	12.2	2.3	9.5
2,5-Di-Me-thiophene	4.9	2.5	1.0	1.1	—	3.5
2-Et-thiophene	11.7	5.1	1.5	?	?	1.2
2,4-Di-Me-thiophene	0.6	1.7	1.5	6.2	3.3	—
2,3-Di-Me-thiophene	1.8	13.6	—	5.1	1.0	0.6
3,4-Di-Me-thiophene	0	1.7	2.3	—	?	2.9
Tri-Me-thiophenes	10.0	8.0	15.0	15.7	15.3	14.2
Others	29.3	18.3	24.0	33.2	17.6	32.1
	100	100	100	100	100	100

<sup>a</sup> The gas chromatographic analyses were carried out without internal standards. The response factors are unknown and the relative errors in the percentages given are probably in the range of  $\pm 10$ –20 %.

(20–40 %) of benzene, but also the two methylthiophenes give significant yields of benzene. Obviously the benzene formation from the latter must occur after methylation to produce the necessary six-carbon precursor.

Demethylation/methylation reactions are indeed observed for all six starting materials. The formation of benzene is formally a result of the loss of the elements of  $\text{H}_2\text{S}$  from the dimethylthiophenes followed by cyclization/rearrangement or vice versa. Also this reaction has a parallel in the glow discharge reaction of phenylthiophenes which lose sulfur and cyclize/rearrange to naphthalene.<sup>1</sup>

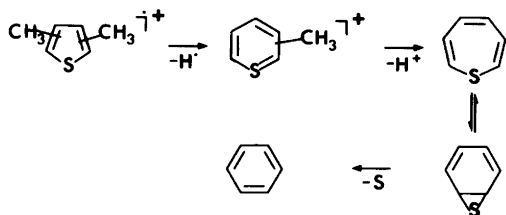
The mechanism for the benzene formation from methylthiophenes must at this stage remain speculative. One possibility is a double ring enlargement with the loss of two hydrogens to produce thiopyrin from which loss of sulfur gives benzene (Scheme 2). Two facts support this mechanism:

1. Ring enlargement of methylthiophenes to thiopyrylium ions is commonly observed under mass spectrometrical conditions. Such conditions have been claimed<sup>16</sup> to be similar to those prevailing in the glow discharge.

2. The fact that all isomeric dimethylthiophenes give benzene in appreciable amounts indicates a mechanism which does not discriminate strongly between the isomers.

## EXPERIMENTAL

The experimental conditions and the glow discharge apparatus have been described earlier.<sup>3</sup> The products from the glow discharge reactions of thiophene were collected in a cooling trap at  $-196^\circ\text{C}$  (liquid nitrogen). The trap was connected to the glass inlet of a mass spectrometer (AEI MS 902) and the product mixture was



Scheme 2. Possible mechanism for the formation of benzene from dimethylthiophenes in a glow discharge.

allowed to warm up to  $-80^\circ\text{C}$  (dry ice/methanol). Mass spectra were recorded at low ionization potential (15 eV) to minimize fragmentation of molecular ions.  $m/e$ -values at 58, 52, 44, 40 and 26 indicated the presence of species with molecular formulas  $\text{C}_2\text{H}_2\text{S}$ ,  $\text{C}_4\text{H}_4$ ,  $\text{CS}$ ,  $\text{C}_3\text{H}_4$  and  $\text{C}_2\text{H}_2$ , respectively.

The liquid products from thiophene and the methylthiophenes were analyzed with GLC/MS. A Hewlett-Packard 5700 A gas chromatograph with a 10 % OV-17 column and a flame ionization detector was used for preliminary analysis. The oven was programmed for a temperature range of  $80^\circ\text{C}$  to  $250^\circ\text{C}$  ( $8^\circ\text{C}/\text{min}$ ). The GLC/MS analyses were carried out at the Central Institute for Industrial Research, Oslo, with a Hitachi Perkin-Elmer RMU GL mass spectrometer and a Perkin-Elmer 990 gas chromatograph. In some cases the AEI MS 902 mass spectrometer from our institute was also used.

## REFERENCES

1. Skramstad, J. and Smedsrud, B. *Acta Chem. Scand. B* 31 (1977) 625.
2. Part of this work was presented at *The Eight International Symposium on Organic Sulfur Chemistry*, Portoroz, Yugoslavia 1978.
3. Fjeldstad, P. E. and Undheim, K. *Acta Chem. Scand. B* 30 (1976) 375.
4. Shoaib Chaudhry, M. *A Study of Some Reactive Intermediates in Low Temperature Plasma (Glow Discharge)*, Cand. Real. Thesis, Oslo 1979.
5. Garvang, A. *A Qualitative Description of Some Alkylthiophenes in Plasma*, Cand. Real. Thesis, Oslo 1976.
6. Bock, H., Solouki, B., Bert, G. and Rosmus, P. *J. Am. Chem. Soc.* 99 (1977) 1663.
7. Howard, E. G., Jr. *U.S. Pat.* 3,035,030 (1962).
8. Maier, L. *Helv. Chim. Acta* 53 (1970) 1216.
9. Reynaud, P., Moreau, R. D. and Samama, J. P. *Bull. Soc. Chim. Fr.* (1965) 3623.
10. McMillan, F. H. and King, J. A. *J. Am. Chem. Soc.* 70 (1948) 4143.
11. Peng, T. C. *J. Phys. Chem.* 78 (1974) 634.
12. Steudel, R. *Z. Anorg. Allg. Chem.* 361 (1968) 180.
13. Dyne, P. J. and Ramsay, D. A. *J. Chem. Phys.* 20 (1952) 1055.
14. Wollrab, J. E. and Rasmussen, R. L. *J. Chem. Phys.* 58 (1973) 4702.
15. Turner, B. E. *Sci. Am.* 228 (1973) 51.
16. Suhr, H. *Angew. Chem.* 84 (1972) 876.

Received September 9, 1983.