

FORMATION OF THIOPHENE BY PYROLYSIS OF DIVINYL SULFOXIDE

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The pyrolysis of divinyl sulfide at 530–550°C leads to the formation of thiophene (48% yield) [1]. We established that divinyl sulfoxide (DVSO) undergoes cyclization at 350–450° to give thiophene (Table 1). The highest yield of thiophene (60%) was obtained at 400°. Besides thiophene are formed water, paraldehyde, hydrogen sulfide, and sulfur dioxide. The yield of paraldehyde increases at 350°, while above 450° the DVSO undergoes profound heat decomposition to give a substantial amount of gaseous products.

It is known that the pyrolysis of *eso*-substituted β -styryl alkyl sulfoxides at 550° leads to the corresponding benzothiophene derivatives [2], as it is assumed, via the intermediate formation of β -styrylsulfonic acid. The thermal decomposition of *tert*-butyl alkyl sulfoxides [3, 4], vinyl β -alkylthioethyl sulfoxides [5], and vinyl β -triorganysilylalkylthio sulfoxides [6] also leads to sulfenic acids.

The character of the thermal decomposition of DVSO in the gas phase and the composition of the formed products testify to its initial conversion to acetylene and vinylsulfonic acid. The thermal dissociation of the latter at the S–O bond leads to the formation of the vinylthiyl radical, which, as was shown by us previously [7], is capable of being converted in the gas phase to thiophene:

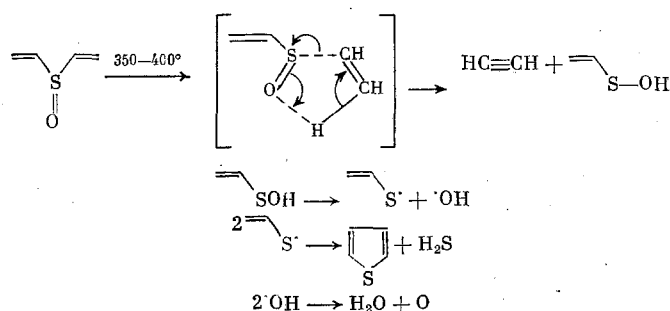


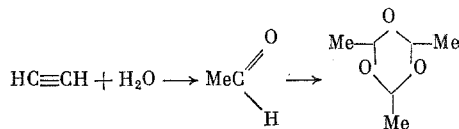
TABLE 1. Gas-Phase Pyrolysis of Divinyl Sulfoxide (DVSO)

| T., °C | Reaction time, min | Weight, g | | Contact time, sec | DVSO conversion, % | Main pyrolysis products and their yield, % | |
|--------|--------------------|---------------|------------|-------------------|--------------------|--|--------------|
| | | starting DVSO | pyrolyzate | | | thiophene | paraldehyde* |
| 450 | 17,5 | 4,7 | 1,8 | 97 | 100 | 34,6 | 1,7 |
| 420 | 4,5 | 2,4 | 1,2 | 66 | 94,2 | 33,5 | 3,2 |
| 400 | 6 | 3,2 | 2,4 | 69 | 87,5 | 60 | 2,4 |
| 380 | 13,5 | 4,5 | 2,5 | 88 | 97,3 | 36,5 | 2,2 |
| 380 | 9 | 4,8 | 2,7 | 68 | 96,3 | 42,8 | 1,8 |
| 350 | 4 | 2,14 | 1,3 | 62 | 89,2 | 26,1 | 19,5 |

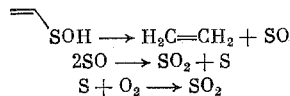
* PMR spectrum (δ , ppm): 1.30 d (CH_3), 4.95 q (CH). Found: C 54.54; H 9.66%; $\text{C}_6\text{H}_{12}\text{O}_3$. Calculated: C 54.54; H 9.09%. The spectrum was obtained on a Tesla 487-BS instrument (80 MHz) using CDCl_3 as the solvent and HMDS as the internal standard.

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Acetaldehyde is apparently formed by the hydration of acetylene and is rapidly trimerized on the cold walls of the trap:



At 450° and higher the vinylsulfenic acid can decompose to give SO₂:



EXPERIMENTAL

The DVSO was pyrolyzed by passing it through an empty quartz tube (560 × 30 mm), placed in an electric furnace, in a nitrogen stream. The condensate was collected in traps cooled to -50° and analyzed by GLC (LKhM-8MD-2 chromatograph, 2 m × 3 mm column packed with 5% Silicone XE-60 deposited on Chezasorb AW-HMDS, carrier gas = helium, and linear programming of the column temperature). The DVSO pyrolysis conditions and yield of the main reaction products are given in Table 1. The gaseous reaction products were analyzed on an LKhM-8MD-5 chromatograph (25% triethylene glycol butyrate deposited on INZ-600).

CONCLUSIONS

The main product of the gas-phase pyrolysis of divinyl sulfoxide at 400° is thiophene (up to 60% yield). Paraldehyde, H₂O, H₂S, and SO₂ are also formed here.

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