Formation of Sulphene by Thermolysis of *N*-Methylsulphonylphthalimide

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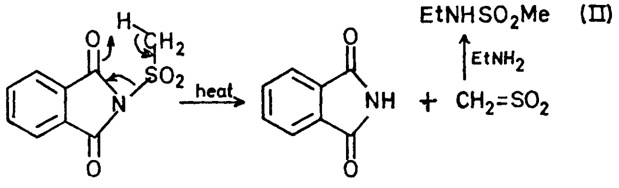
Summary Sulphene (trapped with ethylamine) and phthalimide are fragmentation products from thermolysis of *N*-methylsulphonylphthalimide *in vacuo* at 600 °C; from *N*-benzylsulphonylphthalimide, benzaldehyde and phthalimide were isolated under the same conditions.

Sulphenes are well known as transient species.[1,2] Recently, evidence has been obtained for their existence as discrete species in the gas phase using flash thermolysis.[3–7] It was shown that when sulphene was formed it rapidly underwent further reactions under the conditions used.

By flash thermolysis of chlorosulphonylacetic acid and trapping with MeOD a minimum 12% conversion into sulphene was claimed.†[4] However, only the methyl methanesulphonate obtained (2·6% yield at most) can arise directly from trapping of sulphene.

In the course of our investigations into the thermolysis of *N*-substituted phthalimide derivatives, we found that *N*-methylsulphonylphthalimide (I) is an excellent precursor for the generation of sulphene. When (I) was thermolysed *in vacuo* a quantitative yield of phthalimide was isolated. The other fragment, CH_2SO_2, formulated as a sulphene‡,



(I)

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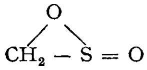
† Although not formulated,[4] the first step in this thermolysis seems to be decarboxylation to methanesulphonyl chloride, which then may form sulphene by losing HCl.[6]

‡ An alternative formulation,[1,3,5]  $\overset{O}{CH_2 - S} = O$ could also account for our gas-phase reactions, but is inconsistent with reported cyclo-additions.[1]

was trapped by ethylamine to give the sulphonamide (II).

This reaction is analogous to the generation of ketens from the corresponding acetylphthalimides,[8] proceeding *via* a six-membered ring transition state[9] and is reminiscent of the decomposition of methanesulphonic acid anhydride.[10]

In a typical experiment (I) was sublimed for 1 h at a constant rate through an unpacked quartz tube at 600° and 0·1 mm. Ethylamine was introduced simultaneously through a capillary after the hot zone. Phthalimide was deposited quantitatively between the oven and this capillary. Pure *N*-ethylmethanesulphonamide (II) condensed directly behind the capillary, 36·6% yield based on (I). The remainder of the pyrolysate, condensed on a cold finger at the end of the apparatus, contained mainly polymeric material and a small amount of unidentified products.

Trapping the sulphene with an ethylamine coating on the cold finger resulted in only 11% yield of *N*-ethylmethanesulphonamide. When methanol was introduced as a trapping agent only trace amounts of methyl methanesulphonate were detected, but large quantities of formaldehyde were formed. Our results confirm that sulphene can exist as a discrete species in the gas phase. It is unstable, tending to decompose into formaldehyde and SO.[3,4] Successful trapping can only be carried out with a very reactive agent introduced directly after generation of the sulphene. We were not able to obtain amine-trapped product from a similar thermolysis of *N*-benzylsulphonylphthalimide at 600 °C. Instead, a quantitative yield of benzaldehyde was obtained. Apparently, phenylsulphene, the expected product, decomposes before reaction with the amine could occur.

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