Photoreactions of Benzene Vapour at 2537Å

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Summary Phenol and mucondialdehyde are the major products during the photolysis of benzene vapour in the presence of oxygen: phenol was also formed in the absence of oxygen by the interaction of irradiated benzene with water.

WE have found that the major products of photolysis of benzene vapour at 2537 Å in the presence of O_2 are phenol and mucondialdehyde. A third product was also formed but was not identified due to its small yield.

A flow through system was used at atmospheric pressure (630 ± 4 Torr) and room temperature. Oxygen was bubbled through benzene *via* a capillary tube and the outgoing gas carried benzene vapour with it. The gaseous mixture of oxygen and benzene was irradiated as it passed through a 2·5 cm diameter silica tube with 2537 Å light from a helical Hanovia lamp. The irradiated gases were then bubbled through a solvent trap. The O_2 flow rate was varied from 5 ml/min to 37·4 l/min, and water, benzene, n-hexane, and cyclohexane were used as trapping solvents.

At low O_2 flow rates phenol was the only product. At high O_2 flow rates (> 15 l/min) and with the organic solvents in the trap, mucondialdehyde was the major product and a minor product which was not phenol was also formed. The minor product had a u.v. spectrum in alkali that indicated the presence of pyrogallol, and gave a red-brown colour with neutral iron(III) chloride in aqueous solution. The colour with iron(II) sulphate was green and not blue as would be expected of pyrogallol.

With water in the trap, phenol was always present at the high flow rates as a minor product even at the highest flow rate. This was indicative of the possible formation of phenol through the interaction of the irradiated benzene with water. To examine this possibility, oxygen free nitrogen was bubbled through benzene and water in the trap at a flow rate of 700 ml/min for 15 h prior to irradiation in order to remove oxygen. On irradiating the N_2–benzene vapour mixture in this O_2 free system for 4 h, phenol was obtained in 0·001% yield. Similar experiments with benzene in the trap instead of water yielded no phenol but a product with λ_{max} 247 nm in hexane which was identified as biphenyl (m.p. 69°).

The distance from the irradiation zone to the solvents in the trap was about 25 cm. Hence, the time taken for the irradiated vapours to reach the solvents in the trap is long compared with the lifetimes of the excited states of benzene. Therefore, the formation of phenol in the O_2 free system must be through an interaction of a long-lived intermediate with water. This intermediate could not be benzvalene since this would react with water to form cyclopenta-1,3-diene-1-carboaldehyde.[1]

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[1] L. Kaplan, L. A. Wendling, and K. E. Wilzbach, *J. Amer. Chem. Soc.*, 1971, **93**, 3821; J. Irina and K. C. Kurien, *Chem. and Ind.*, 1972, 763.