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Short Communication

A semi-micro apparatus for liquid phase photolysis

PETER BORRELL, J. D. HOLMES and J. SEDLAR
Department of Chemistry, University of Keele, Keele, Staffs. (Gt. Britain)
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An apparatus is described for the handling of small volumes of solution in a nitrogen atmosphere. The method is compared with earlier methods involving capillary techniques.

Introduction

Traditional quantitative methods in solution photochemistry suffer the disadvantage of requiring large volumes of reagent and sometimes long irradiation times to achieve an appreciable conversion. Although capillary methods have been devised[1–4] to circumvent the difficulties there are troubles with actinometry in the unfavourable optical system and also variations in concentration between capillary samples when dealing with solutions of involatile compounds. The technique described here was designed to avoid these difficulties while maintaining the advantage of small scale.

The photolysis vessel (Figs. 1 and 2) consists of a cylindrical water-jacketed 'Spectrosil' cell (Ross Scientific Ltd.) 1.3 ml in volume. Nitrogen from a purification line is passed into the cell through a fine stainless-steel needle entering the

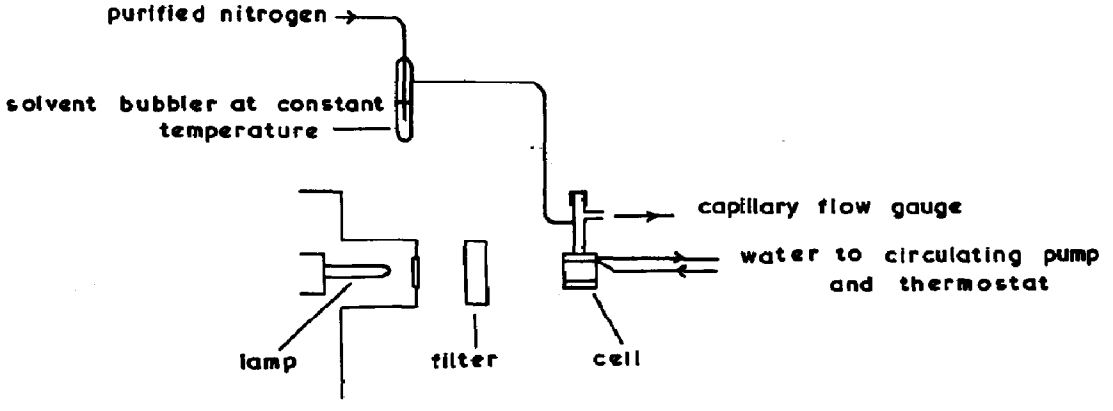

Fig. 1. A diagram of the experimental arrangement.

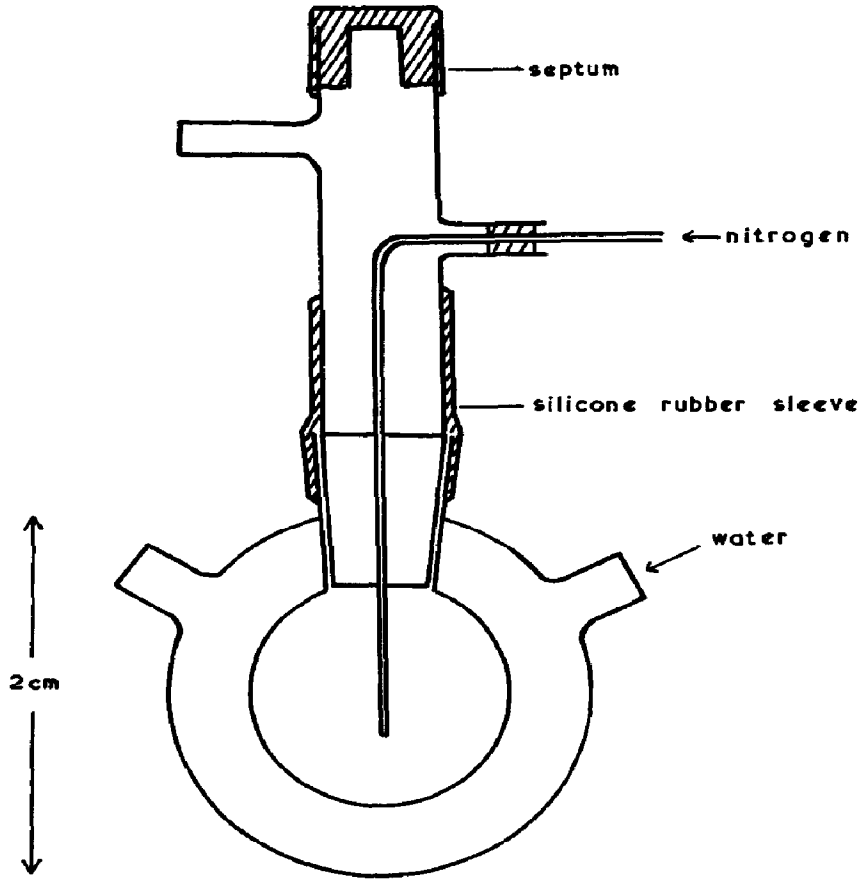

Fig. 2. The photolysis cell.

cell through the side arm of a glass neck attached to the cell by a B7 ground glass joint. Another side arm is connected to a capillary flow meter giving a measure of the nitrogen flow through the cell. The top of the neck is sealed with a silicone rubber serum cap (Fig. 2). Thus, by maintaining a slow flow of nitrogen through the solution being photolyzed, the cell is effectively sealed from the air. The neck is firmly clamped in position on the optical bench whilst the cell can be removed for cleaning. When in use, the cell is supported on a V-shaped rest. The rest of the apparatus consists of a lamp in a brass housing, a suitable optical filter and a thermostat and circulating pump to regulate the temperature in the cell. The whole apparatus, being firmly fixed to a wooden base, was portable.

The nitrogen purification apparatus consists of two parallel glass columns each 25 mm in diameter and 50 cm long surrounded by 'nichrome' heating jackets. Nitrogen from a cylinder (B.O.C. Ltd. 'White spot' grade) is passed up the first column, packed with finely divided copper on Keiselguhr at 170° C, and then down the second column containing activated molecular sieve. The copper packing was

made by depositing copper hydroxide on Keiselguhr (B.D.H. Ltd., acid purified) which was then heated to give cupric oxide. The resulting powder was packed into the column, sealed and activated by passing a stream of hydrogen at 170°C[5]. The active packing material has a violet colour which, as it becomes exhausted, changes to yellow-brown. The column is regenerated with hydrogen after half the packing has changed colour. The molecular sieve was activated under a stream of nitrogen at 180°C. Nitrogen purified in this way should contain under 1 p.p.m. of oxygen[6]. Gas flow through the columns was regulated by a needle valve. Before the nitrogen enters the cell it is saturated with solvent vapour by passing it through a glass bubbling device filled with the solvent being used and maintained at the same temperature as the reaction vessel.

In use the cell is filled with a syringe and fixed to the glass neck using a greased silicone rubber sleeve to ensure an effective seal at the ground joint. A brisk stream of nitrogen is passed for 30 min to de-oxygenate the solution. After the initial period the flow is reduced to about 1 ml min^{-1} which is sufficient to stir the solution and exclude oxygen. Samples can be taken for analysis by gas chromatography with a long-needled microlitre syringe. The few microlitres lost in this way do not appreciably reduce the volume. The method was found to be quite satisfactory for photolysis times of up to 5 h. After this time solvent losses become noticeable.

Since the position of the cell is fixed, chemical actinometry with potassium ferrioxalate[7] can be carried out using the same arrangement. The only change needed is the substitution of a short glass tube and glass capillary for the glass

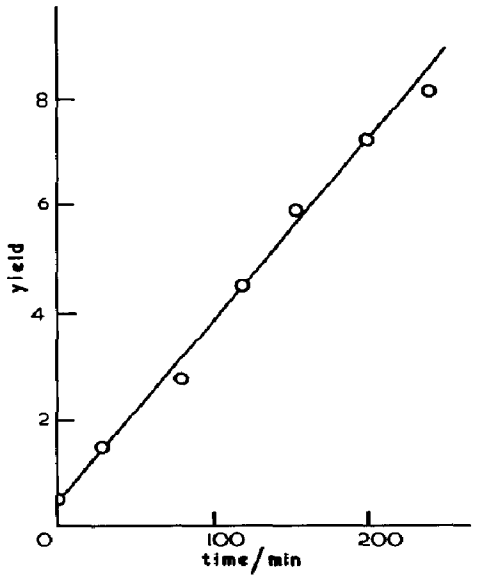

Fig. 3. The production of methyl angelate in the photolysis of methyl tiglate at 254 nm. Concentration of methyl tiglate = 0.035 mole l^{-1} in cyclohexane.

neck and metal needle to avoid the production of spurious Fe^{2+} ions in the actinometer solution.

The major advantages of this semi-micro method over the capillary technique are that the optical path is well defined, the solution is well stirred, solutions of solids can be used and continuous sampling is possible. The disadvantages are that volatile products are lost, very volatile solvents cannot be used and longer irradiation times are required.

A specimen result using this apparatus is shown in Fig. 3. It shows the production of *cis*-isomer from methyl tiglate (*trans*-2-carbomethoxy-2-butene) in the photolysis at 254 nm and 35° C[8]. The solvent was cyclohexane.

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