

Short Communication

High pressure liquid chromatography in photokinetics[†]

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The aims of kinetic analysis are to determine (1) the number of partial reaction steps, together with the number and sequence of reaction products, and (2) the values of the rate constants and/or the photochemical quantum yields of all these partial reaction steps [1]. The rate constants and quantum yields are evaluated from the kinetic differential equations which are determined from the reaction mechanism. A matrix representation of these equations is generally used [1, 2]. The photoproducts are generally unknown in a photokinetic examination. UV and visible (UV-VIS) spectra are often uncharacteristic and overlap in solution. Kinetic analysis by UV-VIS spectroscopy is thus limited to systems obeying the Beer-Lambert law because of the linear dependence between the concentrations of the reactants [1 - 3]. If the absorbances are used in matrix representations, it is no longer possible to distinguish between various mechanisms such as $A \rightleftharpoons B$, $A \rightarrow B$ and $B \leftarrow A \rightarrow C$. In any case partial rate constants cannot be determined unless the absorptivities of all the reactants are known. However, if all the reactants can be selectively traced, the problems arising from the solution of the set of linear kinetic differential equations can be overcome [1, 3]. The specific concentrations rather than the absorbances are then put into the matrix representation. Then the reaction constants can be determined by using eigenvalues.

Conventional chromatographic separation techniques such as gas chromatography and thin layer chromatography have been utilized to support the absorbance measurements. However, these techniques were of limited value because of the low concentrations of reactants used [4]. Therefore the new analytical tool high pressure liquid chromatography (HPLC) was investigated for photokinetic applications. Our intention was to determine the applicability of this new method to a continuous flow system during a photo-reaction. It was expected that more information with respect to the number

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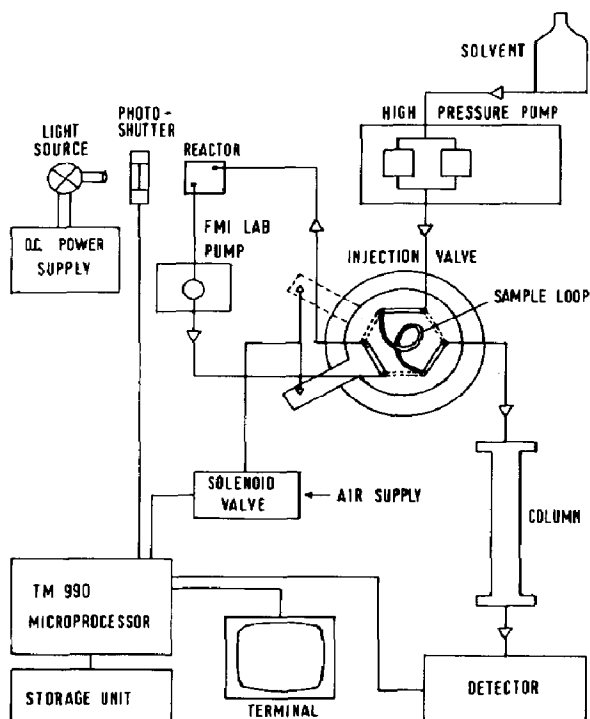


Fig. 1. Block diagram of the HPLC apparatus.

and sequence of products, the mechanism and the absorptivities would be obtained by this method than by absorption spectroscopy alone.

A block diagram of the combined irradiation and analysis apparatus is given in Fig. 1. It consists of an St 75 mercury arc (Quarzlampengesellschaft, Hanau), an automatic valve (Rheodyne), a high pressure pump (Gynkotheke), a Shandon 5 μm ODS Hypersil column (reversed phase C_{18} chain) of dimensions 125 mm \times 4.6 mm and a PMQ II detector system (Carl Zeiss, Oberkochen) including an attachment constructed in the laboratory for the QS 178 microcell (Hellma). A TM 990 microprocessor (Texas Instruments) with a 64 kbyte memory, two floppy disc drives and various input-output interfaces are used to control the shutter and the HPLC system.

The well-known photoreaction of *trans*-stilbene to phenanthrene via *cis*-stilbene ($A \rightleftharpoons B \rightarrow C$) [5] was chosen to test the apparatus. The results are shown schematically in Fig. 2. The absorption of the reactants A, B and C is plotted against the retention time τ on the HPLC column at selected irradiation times t . The time scale is non-linear to optimize the graphical representation with respect to the discrimination of the occurrence of the three reactants. The decrease in the *trans*-stilbene concentration after a short irradiation period agrees with the results shown in the absorbance diagram [5]. The relative heights of the peaks depend on the detection wavelength, which was optimized to 262.5 nm to ensure observation of all three products, and therefore the concentration scale is given in arbitrary units. The advantage over matrix rank analysis [1, 2, 6] is obvious. The number of reactants at each

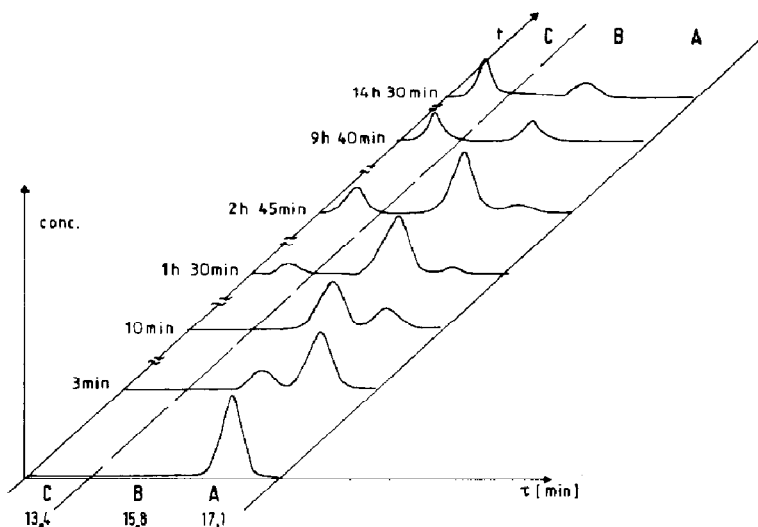


Fig. 2. HPLC spectrum of the stilbene photoreaction (A, *trans*-stilbene; B, *cis*-stilbene; C, phenanthrene). τ is the retention time in minutes.

linear independent reaction step can easily be seen. Therefore HPLC provides an increase in information with respect to the first aim of photokinetic analysis.

The absorptivities of the reactants can be determined either by preparative HPLC or, in simple mechanisms, by the law of conservation of mass. Our simple apparatus could not reach the required standards in photokinetics in the present state of development since the signal was recorded in transmittance using a simple recorder. The use of an analogue-to-digital converter for data acquisition improved microprocessor control and evaluation programs, and a multiwavelength detection system will increase the amount of information obtained and will prove HPLC to be an excellent tool in photokinetics even at concentrations of 10^{-5} M. These improvements are under way and will be reported in a future publication.

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