

Short Communication

Application of graphical matrix rank analysis to flash photolysis

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(Received March 17, 1982)

The graphical methods for matrix rank analysis developed by Mauser [1 - 3], in particular the use of extinction (E), extinction difference (ED) and extinction difference quotient (EDQ) diagrams, have found many applications in the analysis of photokinetics. Although they have also been used in the analysis of chemical equilibria and the kinetics of purely thermal reactions, to the best of our knowledge these methods have not been applied to flash photolysis. The aim of this communication is to demonstrate the advantages of applying E, ED and EDQ diagrams to flash kinetic spectroscopy.

If the kinetic curves obtained at a number of different wavelengths or the spectra obtained at a number of delay times of increasing length after the photolysis flash are arranged to form a matrix ΔE_{nm} where n denotes the number of wavelengths and m the number of samples per curve, then the rank of this matrix is equal to the number of independent reactions proceeding in the system. This has been discussed by Ainsworth [4] for closed and open reacting systems. The numerical methods for the determination of the rank make use of repeated matrix rearrangements (pivotal element selection) in order to minimize the propagation of experimental errors [5 - 7]. The information lost by these rearrangements can often be obtained in a straightforward manner by graphical analysis.

The principle is simple. One column of the ΔE matrix is chosen as the abscissa and all the other columns are plotted against it (ED diagrams). The rank is unity if all plots are linear within the limits of experimental error. If at least one significant deviation from linearity occurs, the rank of the matrix is reduced by dividing all elements by the corresponding element of one particular column and the plotting procedure is repeated (EDQ diagrams). In principle this procedure could be continued *ad infinitum* but the limits of experimental accuracy do not usually allow ranks r greater than 2 to be determined with certainty. In flash photolysis the extinction difference is usually obtained rather than extinction itself, and thus the subtraction of one row from all the others can be omitted in the first rank reduction step. So far the graphical analysis is completely equivalent to the numerical method, especially if the error matrix is also calculated and the individual

points are plotted together with their corresponding uncertainties. Pivotal element selection in the numerical procedure is equivalent to an appropriate choice of the rows and columns for the subtractions and divisions and for the abscissa in the graphical analysis.

The advantage of the graphical method is that valuable information on the particular kinetic scheme of the system studied can be extracted. It is usually possible to predict some properties of the diagrams, *e.g.* the initial or final slopes of non-linear ED diagrams, and the intercepts and coordinates of the first and final points in EDQ and other diagrams, even if the individual extinction coefficients, rate constants and initial concentrations are only partially known, or to predict a possible dependence of these quantities on dilution or changes in the initial concentrations. Comparison with the experimental results enables the proposed reaction mechanism to be confirmed or rejected, which cannot be done from a knowledge of the rank alone. A more detailed discussion of this technique is given by Mauser [3].

Manual graphical analysis is a tedious procedure, and wrong conclusions may be drawn if only a few diagrams are considered. Therefore we have developed a dialogue program for a desk calculator (EMG 666, 8 kbyte plus an external 16 kbyte random access memory) connected to a plotter which allows all possible diagrams to be plotted in a very short time. A graphical display would be even more convenient, at least for an initial visual inspection. On-line coupling to the recording system of our flash photolysis apparatus is in preparation. It should be emphasized that precise reproducibility of the experimental conditions is necessary if the kinetic data are recorded in successive shots. A multichannel recording system is preferable.

Figures 1 - 3 show a representative selection of transient ΔE spectra, ED diagrams and EDQ diagrams obtained from 21 kinetic curves in the wavelength region 300 - 510 nm ($m = 30$). The sample was a solution of 1.72×10^{-5} M bromothymol blue and 4.37×10^{-4} M pyridine in toluene.

A generalized kinetic scheme for this type of reaction has been proposed [8, 9]. In the particular case discussed here the reaction mechanism should be obtainable by simplification of the scheme

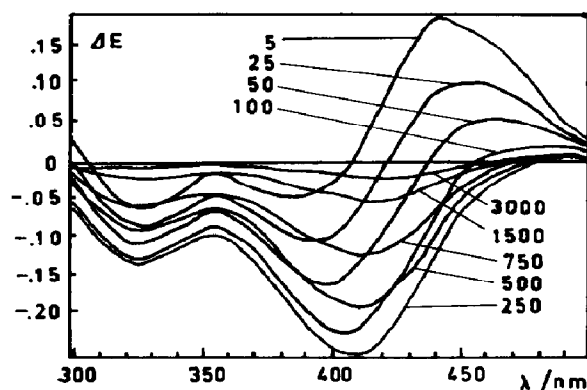
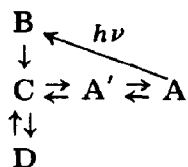


Fig. 1. Transient spectra at the delay times indicated (in milliseconds). ΔE is the extinction difference.



The non-absorbing species D cannot be neglected owing to the existence of temporary bleaching over the entire wavelength range. The $B \rightarrow C$ reaction was too fast for the time resolution of our conventional flash photolysis apparatus. Since the initial slope of the ED diagrams almost vanishes in the region where the extinction coefficient of the final form A approaches zero it must be concluded that A is formed in a consecutive rather than a parallel reaction. Taking into account the rank $r = 2$ (linear EDQ diagrams) the correct scheme must read

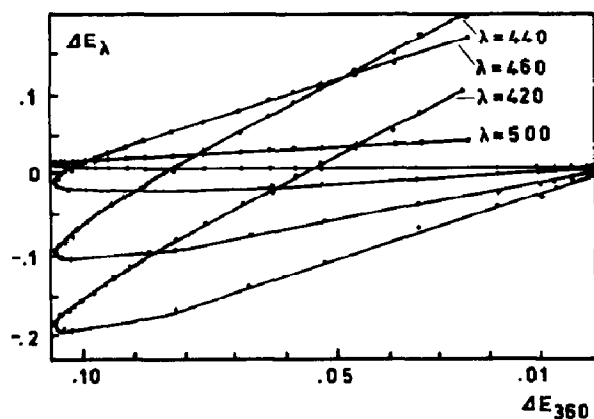


Fig. 2. ED diagrams (λ is in nanometres).

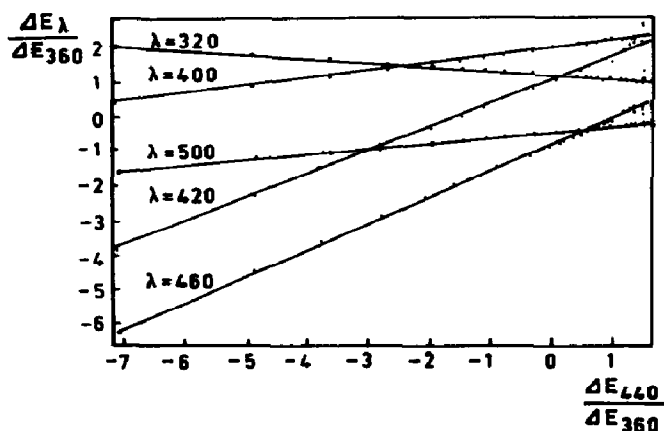


Fig. 3. EDQ diagrams (λ is in nanometres).

The two linear parts of the ED diagrams show that in the initial period of the reaction the establishment of the equilibrium $C \rightleftharpoons D$ is much faster than the competitive reaction $C \rightarrow A$, whereas later the reaction $C \rightarrow A$ becomes the dominant step and C and D remain in equilibrium.

We were able to determine all the rate constants and extinction coefficients involved by a least-squares fitting procedure. The theoretical ΔE matrix was calculated from these parameters and the theoretical and experimental diagrams were proved to be identical within the limits of experimental error. Four alternative reaction schemes were ruled out.

In summary we conclude that computer-aided graphical methods of matrix rank analysis are a useful tool in the interpretation of flash photolysis experiments if complicated kinetics are observed. They provide more information than do the purely numerical procedures. The computational effort is small and the error analysis is straightforward.

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