

A QUANTITATIVE APPROACH TO THE ANALYSIS OF BIEXPONENTIAL DECAY CURVES IN FLASH PHOTOLYSIS[†]

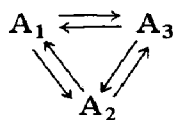
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Summary

A method which allows the determination of all rate constants, initial concentrations and extinction coefficients in a chemical system with three constituents coupled by first-order reactions is developed. The only condition required is that the spectra of one species and of the equilibrated system are known or that one species does not absorb in the spectral region under investigation. The method has been successfully used to discriminate between all possible kinetic schemes which can be derived from the cyclic scheme



Generalization to multiexponential decays is discussed.

1. Introduction

The solutions of the set of differential equations

$$\frac{d}{dt} \mathbf{A} = \mathbf{K} \mathbf{A}$$

describing any complex system of coupled first-order (or pseudo-first-order) reactions can always be written in the form

$$A_{i(t)} = \sum_{j=1}^n a_{ij} \exp(-\theta_j t) \quad (1)$$

where $A_{i(t)}$ is the concentration of the i th component as a function of time and n is the total number of constituents. The θ_j are the eigenvalues of the kinetic matrix \mathbf{K} , and they can be expressed as algebraic functions of the rate constants alone although this may be difficult for large systems. The

[†] Dedicated to the late Professor Dr. R. Paetzold.

pre-exponential factors a_{ij} are generally functions of both the rate constants and the initial concentrations. A detailed description of the eigenvalue problem in first-order kinetics with special emphasis on the formal mathematical analogy with normal coordinate analysis has been given by Matsen and Franklin [1]. In order to obtain the optical density D_ν at the wavelength ν as a function of time eqn. (1) must be expressed as a linear combination with the molar absorptivities as coefficients:

$$D_{\nu(t)} = \sum_{i=1}^n \epsilon_{\nu i} A_i(t) \quad (2)$$

If the change in the absorbance

$$\Delta D_{\nu(t)} = D_{\nu(t)} - D_{\nu(t \rightarrow \infty)}$$

is recorded, as is usually the case in flash photolysis, the kinetic rate law is given by

$$\Delta D_{\nu(t)} = \sum_{j=1}^{n-1} d_{\nu j} \exp(-\theta_j t) \quad (3)$$

where

$$d_{\nu j} = \sum_{i=1}^n a_{ij} \epsilon_{\nu i}$$

One eigenvalue θ in eqn. (1) must be zero as a consequence of mass conservation in a closed system and the constant term cancels owing to the use of the difference ΔD_ν ; thus the summation is over $n - 1$ rather than n .

The eigenvalues θ_j and the corresponding pre-exponential factors $d_{\nu j}$ are obtained by fitting the experimentally obtained kinetic curves to eqn. (3). This gives a system of $2(n - 1)$ algebraic equations from which the rate constants are to be extracted. As long as there are $n - 1$ unknown rate constants this procedure is straightforward. However, in the more general case the number of unknown rate constants exceeds the number of eigenvalues. Since in flash photolysis the initial concentrations immediately after the flash and the extinction coefficients of the transients are usually unknown it is impossible to solve the inverse kinetic eigenvalue problem without additional independent information. In other words it is necessary to solve the matrix equations

$$(\theta \mathbf{E} - \mathbf{K}) = \mathbf{0}$$

(\mathbf{E} is the unit matrix) where only θ is known and

$$\mathbf{d} = \mathbf{a} \boldsymbol{\epsilon}$$

where only \mathbf{d} is known and \mathbf{a} contains the unknown initial concentrations and the elements of \mathbf{K} . This is a typical poorly posed problem but it is not

trivial even for $n = 3$. It is the purpose of this paper to show how this problem of underdetermination can be overcome by analysing the kinetic curves at a sufficiently large number of different wavelengths. In particular we shall demonstrate the determination of all rate constants, extinction coefficients and initial concentrations of the transients for the scheme



2. Analysis of system (4)

The expressions for the eigenvalues θ_1 and θ_2 and the pre-exponential factors d_{ν_1} and d_{ν_2} were obtained from the general solution given in ref. 2 for the three-membered cyclic system by neglecting k_{23} and k_{32} :

$$\theta_{1,2} = \frac{1}{2} (k_{12} + k_{21} + k_{13} + k_{31}) \pm \left\{ \left(\frac{k_{12} - k_{21} + k_{13} + k_{31}}{2} \right)^2 + k_{12}(k_{21} - k_{31}) \right\}^{1/2} \quad (5)$$

$$d_1 = \frac{k_{12}(1 - \lambda_1) + k_{13} + k_{31}}{(\lambda_1 - \lambda_2)\theta_1} A_{1(0)} - \frac{\{k_{21}(1 - \lambda_1) - k_{31}\}A_{2(0)} + k_{31}C_0}{(\lambda_1 - \lambda_2)\theta_1} \times \\ \times \left[\epsilon_{app} \frac{k_{13} + k_{31}}{k_{13}} (\lambda_2 - 1) - \epsilon_1 \left\{ \frac{k_{31}}{k_{13}} (\lambda_2 - 1) + \lambda_2 \right\} \right] \quad (6)$$

$$d_2 = \frac{k_{12}(1 - \lambda_2) + k_{13} + k_{31}}{(\lambda_1 - \lambda_2)\theta_2} A_{1(0)} - \frac{\{k_{21}(1 - \lambda_2) - k_{31}\}A_{2(0)} + k_{31}C_0}{(\lambda_1 - \lambda_2)\theta_2} \times \\ \times \left[\epsilon_1 \left\{ \frac{k_{31}}{k_{13}} (\lambda_1 - 1) + \lambda_1 \right\} - \epsilon_{app} \frac{k_{13} + k_{31}}{k_{13}} (\lambda_1 - 1) \right] \quad (7)$$

where

$$\lambda_1 = \frac{k_{21} - k_{31}}{k_{21} - \theta_1}$$

$$\lambda_2 = \frac{k_{21} - k_{31}}{k_{21} - \theta_2}$$

and $C_0 = [A_1] + [A_2] + [A_3]$ is the total analytical concentration.

In the particular case investigated here the extinction coefficient ϵ_2 is known to be zero over the entire spectral range under investigation. An apparent extinction coefficient

$$\begin{aligned}\epsilon_{\text{app}} &= \frac{\epsilon_1[A_1]_e + \epsilon_3[A_3]_e}{[A_1]_e + [A_3]_e} \\ &= \frac{k_{31}}{k_{12} + k_{21}} \frac{1}{k_{13} + k_{31}} (k_{31}\epsilon_1 + k_{13}\epsilon_3)\end{aligned}\quad (8)$$

and an equilibrium constant

$$K_e = \frac{[A_1]_e + [A_3]_e}{[A_2]_e} = \frac{k_{21}}{k_{12}} \left(1 + \frac{k_{13}}{k_{31}} \right) \quad (9)$$

can be defined for the equilibrated system. Since it is possible in this special case to shift the equilibrium so far to the right that $[A_2]_e$ becomes negligible (k_{21} has been proved to be a pseudoconstant) ϵ_{app} can also be measured under the condition $k_{21} \gg k_{12}$ which makes the determination of K_e straightforward. It should be emphasized that a knowledge of K_e is not absolutely necessary for the analysis described here (see below). A more detailed interpretation of the experimental results is given elsewhere [3, 4].

In the first stage of the analysis the kinetic curves measured at a number of different wavelengths in a spectral region chosen as broad as possible are fitted to the biexponential rate law in order to obtain the matrix d and the eigenvalues θ_j together with their standard deviations. The weighted mean of the eigenvalues is calculated using the reciprocal variances of the individual θ_{vj} as statistical weights. It should be noted that the biexponential model can only be used if there is no systematic variation in the θ_{vj} with the wavenumber of the analysis.

In an alternative approach which needs much less computational effort we first add all the kinetic curves digitized at identical times and obtain the eigenvalues from a single fitting of the accumulated kinetic curve. Then the elements of the matrix d can be calculated using a linear regression method. It is obvious that this simplified procedure cannot be used if one or both pre-exponential factors changes its sign at some wavenumber and the sum becomes very small, *i.e.* one or even both of the exponentials may vanish in the kinetic curve accumulated over various analysis wavelengths. In the next step eqns. (5) for the eigenvalues θ_1 and θ_2 are used to calculate the total possible range for the set of rate constants by assigning arbitrary but reasonable values to as many rate constants as necessary to make the system of equations solvable. From the condition that all rate constants have to be real and positive it follows that the solutions exist over only a comparatively small finite range.

In the particular case investigated here we have two eigenvalues and four unknown rate constants. The additional eqn. (9) for the equilibrium constant reduces the number of optional rate constants to one. Obviously an upper limit $k_{nm} < \theta_1 + \theta_2$ exists for all rate constants; furthermore there is a lower limit for k_{31} which is readily detected by the appearance of complex solutions for some of the remaining constants. Figure 1 shows the result of this calculation.

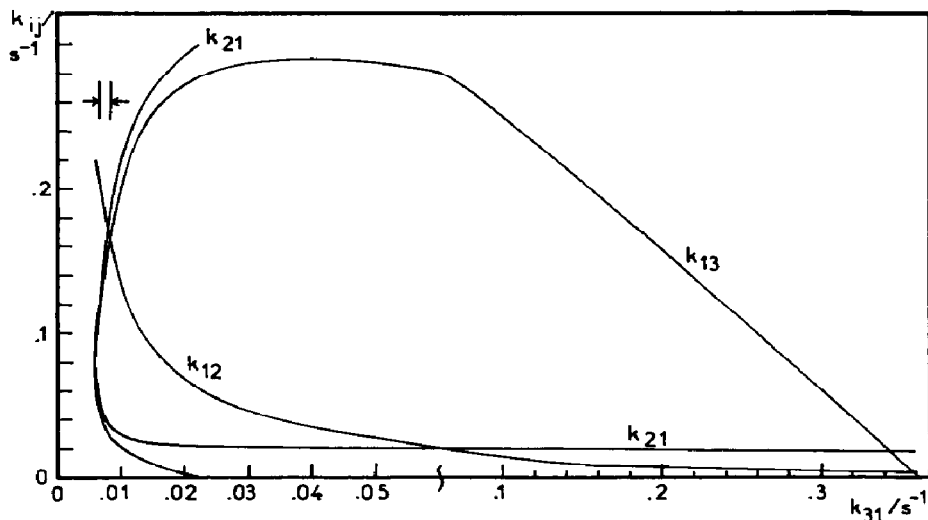


Fig. 1. Plot of k_{12} , k_{21} and k_{13} as functions of k_{31} .

In the third step of data processing we calculate the initial concentrations $[A_1]_0$ and $[A_3]_0$ and the extinction coefficients ϵ_1 and ϵ_3 from the analytical expressions for the pre-exponential factors to find a region in the field of rate constants for which the following reasonable initial concentrations and extinction coefficients can be obtained:

$$0 < [A_i]_0 < C_0 \quad 0 < \epsilon_{\nu i}$$

When a physically reasonable solution is obtained it is improved further by trial and error until the calculated initial concentrations are independent of the wavenumber of the analysis. This is indicated by a vanishing correlation coefficient for the plot of $[A_i]_0$ versus the wavenumber. A vanishing correlation coefficient is a necessary but not a sufficient condition for the optimal solution. Statistical criteria derived from testing "runs above and below the median" and "runs up and down" [5] must also be fulfilled, but they have been found to be unsatisfactory for discriminating between solutions close to the optimum solution.

A "theoretical" matrix d can be calculated from the optimized solution for the rate constants, extinction coefficients and the averaged initial concentrations to obtain the weighted sum of the squared residuals:

$$S = \sum_{j=1}^{n-1} \sum_{\nu} w_{\nu j} (d_{\nu j, \text{calc}} - d_{\nu j, \text{exp}})^2$$

The weights $w_{\nu j}$ are the reciprocal variances of $d_{\nu j, \text{exp}}$ obtained from the biexponential fit to the individual decay curves. We now determine whether S reaches a minimum for small variations in the adjusted parameters. If the analytical expressions for the general three-membered cyclic scheme are used for this purpose it is easy to determine whether the neglect of particular rate constants is justified or whether the fit can be improved by assigning

finite values to them. If more than one kinetic scheme gives a physically meaningful solution then the scheme with the smallest value of S should be taken as the most probable.

3. Experimental details

The chemical system consisted of 1.23×10^{-5} M of bromoxylenol blue in toluene in the presence of 3.12×10^{-3} M pyridine. A_2 is the colourless sultone, and A_1 and A_3 are two forms of the yellow open-ring compound. Bromoxylenol blue was purchased from Fluka and was used without further purification. The flash apparatus was the same as that briefly described in ref. 4. The photolysis cell was thermostatted to about 0.2°C . The solution was flashed repeatedly since exactly reproducible curves were obtained even after 20 flashes if the sample was allowed to equilibrate thermally for 10 min after each flash. The kinetic curves were recorded at 21 wavelengths.

All the calculations were performed using an EMG 666 desk calculator.

4. Results and discussion

Figure 2 shows a set of transient spectra obtained experimentally. The values $\theta_1 = 36.2 \pm 1.3 \text{ s}^{-1}$ and $\theta_2 = 2.24 \pm 0.10 \text{ s}^{-1}$ were calculated from the cumulative kinetic curves. The experimental factors $d_{\nu,j}$ are shown in Fig. 3 together with those calculated from the final solution. Figure 1 shows the graph of the dependence of k_{12} , k_{21} and k_{13} on the arbitrarily chosen k_{31} . The range over which positive extinction coefficients and positive initial concentrations are calculated for all kinetic curves is indicated. It is also remarkable that only one of the two roots for k_{21} and k_{13} fulfils the conditions given above. Table 1 shows the results of the linear regression $[A_1]_0$ versus wavelength for some sets of rate constants together with the sum of

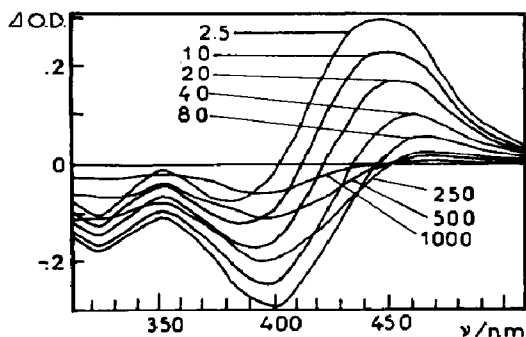


Fig. 2. Set of transient spectra constructed from the kinetic curves. The numbers on the curves give the delay times in milliseconds.

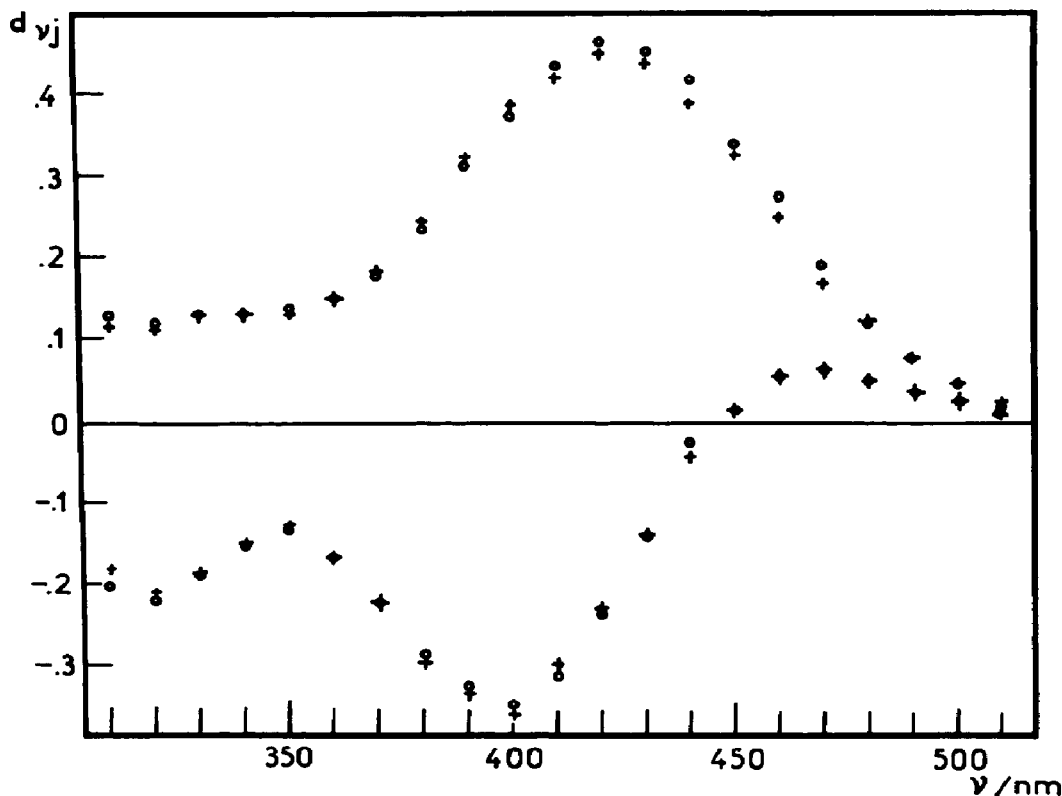
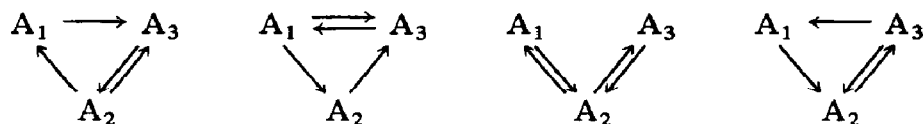


Fig. 3. Plot of the pre-exponential factors $d_{\nu j}$ vs. wavelength; +, experimental data; o, calculated from the final solution.

the squared residuals. Because the relative error p_{rel} of the pre-exponential factors was found to be approximately constant in this example ($2\% < p_{\text{rel}} < 4\%$) $w_{\nu j}$ was set equal to $d_{\nu j}^{-2}$ for simplicity. It can be seen that the minimum for r coincides well with that for S .

Furthermore the fit is not improved by either varying K_e slightly or including k_{23} or k_{32} . Figure 4 shows the spectra of the components from four independent runs.

We have also attempted to use the same method to fit the experimental data to the following models:



Since an interchange of A_1 and A_3 in the schemes only means an arbitrary change in the labelling, obviously no further schemes exist which contain four or less rate constants and which allow all constituents to remain in equilibrium. It has been found that there is no set of positive rate constants which is consistent with the initial concentrations $0 < [A_1]_0 < C_0$ and positive extinction coefficients throughout the entire spectral region.

TABLE 1

The correlation coefficient r for the linear regression $[A_1]_0$ versus ν and the squared sum of the residuals within the acceptable limits of the rate constants

k_{12}	k_{21}	k_{13}	k_{31}	r	S
20.7	12.2	4.86	0.660	-0.76	51.03 ^a
19.8	13.7	4.22	0.690	-0.51	2.287
19.5	14.1	4.06	0.700	-0.34	1.284
19.3	14.5	3.92	0.710	-0.10	0.893
19.2	14.7	3.88	0.713	0.01	0.843
19.0	14.9	3.79	0.720	0.18	0.808
18.7	15.3	3.67	0.730	0.42	0.897
18.2	16.0	3.46	0.750	0.71	1.378
17.1	17.5	3.65	0.800	0.88	3.527
16.1	18.8	2.74	0.850	0.91	6.598 ^b
19.8	13.8	4.12	0.720	ND	1.616 ^c
18.2	15.9	3.53	0.720	ND	1.051 ^d
19.0	15.0	3.61	0.720	ND	0.889 ^e
16.3	18.5	2.83	0.720	ND	5.656 ^f

ND, not determined.

^aUnreasonable solution because ϵ_3 is less than zero for $\nu \geq 500$ nm.

^bUnreasonable solution because $[A_1]_0$ is greater than C_0 for $\nu \geq 490$ nm.

^c K_e was 5% less than the experimental value.

^d K_e was 5% greater than the experimental value.

^e $k_{23} = 0.1$; $k_{32} = 0$.

^f $k_{32} = 0.1$; $k_{23} = 0$.

Thus an unequivocal distinction has been made between all alternative kinetic schemes which lead to the same form of rate law. This result confirms the conclusion drawn from the corresponding extinction difference diagrams [6].

5. General conclusions

If we consider a system of n chemical constituents coupled by (pseudo-) first-order reactions we may have as many as $n(n - 1)$ unknown rate constants. There are $n - 1$ equations relating the experimental eigenvalues of the kinetic matrix to the rate constants. A further $n - 1$ equations are available from the prefactors of the exponential terms; these equations contain an additional $n - 1$ unknown extinction coefficients and the unknown initial concentrations. One extinction coefficient or a weighted mean should always be measurable in an equilibrated system. The recording of the kinetic curve at any further wavelength provides $n - 1$ new equations for the pre-exponential factors which also contain $n - 1$ new unknown extinction coefficients. Consequently if the spectrum of one of the species involved is known in

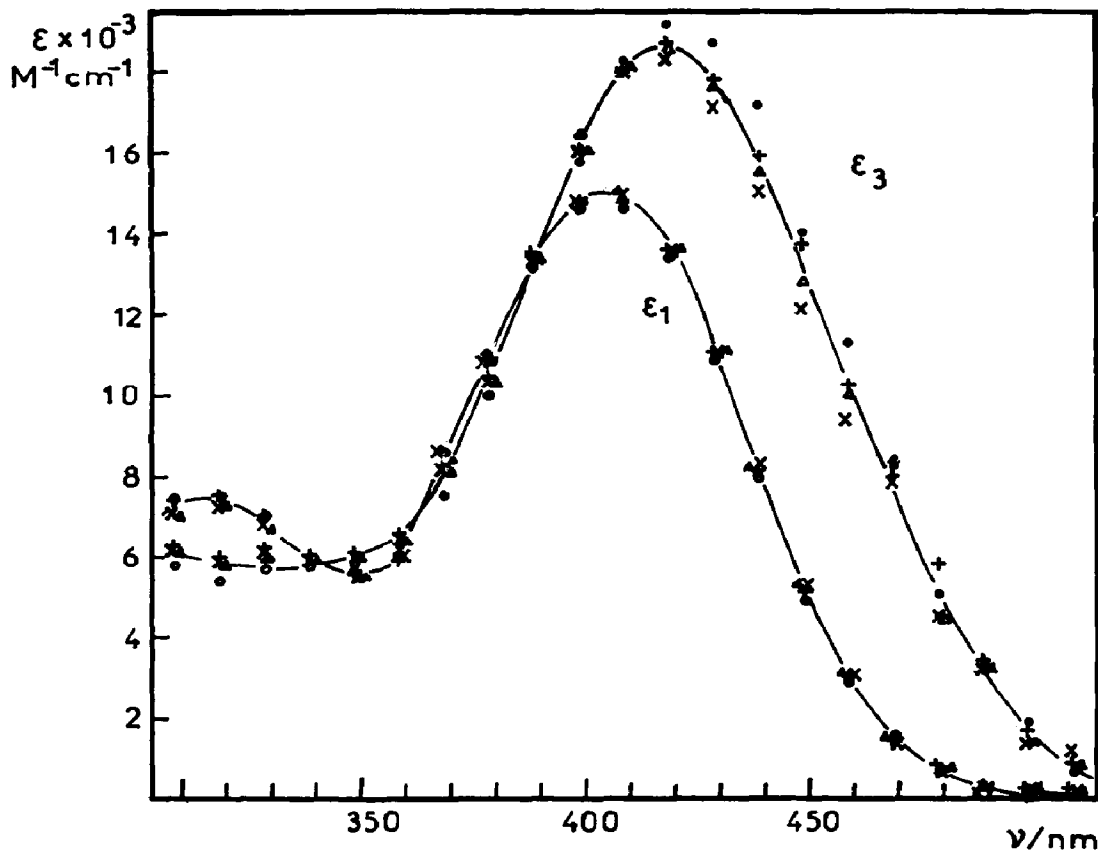


Fig. 4. Spectra of the components A_1 and A_3 calculated from four independent runs.

addition to the spectrum of the equilibrated system then in principle all the unknowns can be determined from the flash kinetic data alone if the kinetic curves are recorded at a sufficient number of different wavelengths. Of course, limited experimental accuracy introduces restrictions. General statements about the accuracy required cannot be made because it strongly depends on the relative magnitudes of the individual rate constants as well as on the spectral properties of the species involved in the system under investigation. An unfavourable situation is indicated by the rank analysis of the corresponding density matrix [6].

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