Photophysics and Kinetics of Naphthopyran Derivatives, Part 3: A General Procedure to Uniquely Identify the Kinetic and Spectroscopic Parameters of ABC($2k$,2ϕ) Systems and Application to Naphthopyran Reactions

M. MAAFI,[1] R. G. BROWN[2]

[1] *Leicester School of Pharmacy, De Montfort University, The Gateway, Leicester,* LE1 9BH, UK
[2] *School of Applied Sciences, University of Glamorgan, Pontypridd, Rhondda Cynon Taff, Cardiff,* CF37 1DL, UK

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ABSTRACT: A new procedure has been developed with the aim of determining the kinetic and spectroscopic parameters of any photochemical systems of the generic ABC($2k$,1ϕ) and ABC($2k$,2ϕ) types. General expressions of the colorability and the equilibrium concentration ratio of two (of the three involved) species at a photostationary state or a state of thermal equilibrium have been derived. The procedure has been successfully applied to achieve unique identifiability for the seven sequences of the ABC($2k$,1ϕ and 2ϕ) type that may represent naphthopyran dynamics. It is demonstrated that the reactivity of this particular compound is certainly described by a higher kinetic level than those (three or four reaction steps) considered in the present study. © 2006 Wiley Periodicals, Inc. Int J Chem Kinet 38: 421–430, 2006

Parts 1 and 2 of this series are references [1] and [2].

Correspondence to: Mounir Maafi; e-mail: mmaafi@dmu.ac.uk.

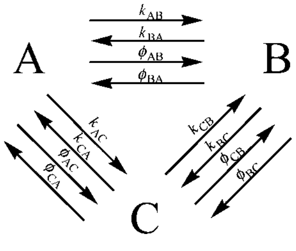
INTRODUCTION

Many photochemical systems involving three reactive species are characterized by three or four reaction steps including two thermal processes and one or two photochemical reactions [3–9]. These can symbolically be named as ABC($2k$,2ϕ) systems. Theoretically, the simplest ABC($2k$,1ϕ) systems are dependent on eight variables, i.e. two rate constants, a photochemical yield, two molar absorption coefficients and three concentrations at the photostationary state, if we consider that the spectral features of one compound are known as well as the initial concentrations of all individual species. Frequently, these system constants are not accessible to measurement and neither are the spectra of all the species involved. Consequently, analysis of the photochemical reaction is practically very demanding; so that, to determine the set of parameters, the approaches proposed generally necessitate the introduction of assumptions [3–9].

In this study, for the first time we propose a general procedure aiming to analytically solve the kinetics of such systems without introducing any simplifications. Furthermore, only one set of parameters is generated because the method offers the possibility to achieve unique identifiability for each of the sequences considered. In the second part of the paper, we apply the procedure to investigate the kinetics of the photochrome 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran.

FUNDAMENTAL BASIS

The basic model showing the total number of photochemical and thermal reactions that can link three species together is shown in Scheme 1. The solution of any ABC($2k$,2ϕ) mechanism extracted from the basic model will be achieved progressively in four steps. The theoretical description of the kinetic model and all the expressions used here to set out the general procedure are based on the formalism developed previously for ABC(nk,$m\phi$) systems [1]. The reader is therefore referred to reference [1] for the derivation of the equations used in this paper. The irradiation of the solution is conducted using monochromatic light whose wavelength corresponds to that of an isosbestic point. We also assume that a true photostationary state is attainable within a reasonable time period. In the subsequent treatment the labeling of all the parameters is carried out in conformity with that used in previous studies [1 and 2] except when otherwise specified.



Scheme 1 General model from which ABC($2k$,2ϕ) systems are extracted.

We will consider two separate situations, namely where the system is being irradiated or where the irradiation light is switched off and only thermal processes operate. The quantities related to the photochemical reaction are throughout denoted by the subscript "P" and those characterizing the thermal reaction, when the irradiation light has been removed, are denoted by the letter "T." The photostationary state is referred to by the symbol "PSS," a state of thermal equilibrium by "STE" and initial quantities by the superscript or subscript "0". Changes in concentration of one or more of the species during the course of the reaction are monitored at an observation wavelength λ_{obs} nm.

In the present procedure it will be assumed that the experimentalist knows the total initial concentration (C_0) of the starting compounds (Eq. (1)).

$$C_0 = C_A^0 + C_B^0 + C_C^0 = C_A(t) + C_B(t) + C_C(t) \quad (1)$$

The rate constants and photochemical yields involved in the various ABC($2k$,2ϕ) mechanisms are denoted respectively, k_a, k_b and ϕ_c, ϕ_d (where the a–d indexes correspond each to a couple of capital letters as depicted in Scheme 1). For each possible mechanism it is necessary to define the basic kinetic coefficients a_{1-9} as given by Eqs. (2) [1]. The $a_{i\text{P}}$ coefficients are obtained from Eqs. (2) by setting all k_i and ϕ_i values to zero except for the four reaction steps involved in the mechanism under consideration. The coefficients representing the thermal reactions ($a_{i\text{T}}$) are similar to the $a_{i\text{P}}$ ones but with all quantum yields set to zero. The light constant γ is defined experimentally.

$$a_{1(\text{P,T})} = -k_{AB} - \phi_{AB}\cdot\gamma - k_{AC} - \phi_{AC}\cdot\gamma \quad (2.1)$$

$$a_{2(\text{P,T})} = k_{BA} + \phi_{BA}\cdot\gamma \quad (2.2)$$

$$a_{3(\text{P,T})} = k_{CA} + \phi_{CA}\cdot\gamma \quad (2.3)$$

$$a_{4(\text{P,T})} = k_{AB} + \phi_{AB}\cdot\gamma \quad (2.4)$$

$$a_{5(\text{P,T})} = -k_{BA} - \phi_{BA}\cdot\gamma - k_{BC} - \phi_{BC}\cdot\gamma \quad (2.5)$$

$$a_{6(\text{P,T})} = k_{CB} + \phi_{CB}\cdot\gamma \quad (2.6)$$

$$a_{7(\text{P,T})} = k_{AC} + \phi_{AC}\cdot\gamma \quad (2.7)$$

$$a_{8(\text{P,T})} = k_{BC} + \phi_{BC}\cdot\gamma \quad (2.8)$$

$$a_{9(\text{P,T})} = -k_{CB} - \phi_{CB}\cdot\gamma - k_{CA} - \phi_{CA}\cdot\gamma \quad (2.9)$$

$$\gamma = F\cdot l\cdot I_0\cdot\varepsilon_{\text{isos.}} = \text{constant} \quad (2.10)$$

We proceed now to the description of the individual steps of the procedure for a single hypothetical sequence ABC(k_a, k_b, ϕ_c, ϕ_d). Each step is aimed at deriving one or more of the unknown parameters that are subsequently used in the next step(s).

Step 1: Defining the Rate Constants

The data collected from the separate photochemical and thermal experiments are individually fitted by the model Eq. (3.1). We stress here that the procedure is exclusively applicable to those sequences which do not include a reversible thermal process linking two of the three species. This work will consider bi-exponential kinetic traces and a general treatment for ABC($2k$,2ϕ) mechanisms, and hence, simpler cases can easily be worked out from this procedure.

According to the formalism [1] the photochemical and thermal overall reactions of any ABC($2k$,2ϕ) sequence are classified in Cases I and II and well described by Eq. (3.1).

$$M^{\lambda}_{(\mathrm{P,T})}(t) = -\frac{m^{\lambda}_{0(\mathrm{P,T})} - M^{\lambda}_{0(\mathrm{P,T})}\cdot\vartheta_{-(\mathrm{P,T})}}{\vartheta_{-(\mathrm{P,T})} - \vartheta_{+(\mathrm{P,T})}}\cdot e^{\vartheta_{+(\mathrm{P,T})}\cdot t} + \frac{m^{\lambda}_{0(\mathrm{P,T})} - M^{\lambda}_{0(\mathrm{P,T})}\cdot\vartheta_{+(\mathrm{P,T})}}{\vartheta_{-(\mathrm{P,T})} - \vartheta_{+(\mathrm{P,T})}}\cdot e^{\vartheta_{-(\mathrm{P,T})}\cdot t} + \theta^{\lambda}_{4(\mathrm{P,T})} \tag{3.1}$$

where M_0 and m_0 represent the initial absorbances and rates of the reactions, and the θ_4 coefficients are constants defined at a specific wavelength. The overall thermal rate constants are given by the following expressions [1]:

$$\vartheta_{\pm(\mathrm{P,T})} = 0.5\cdot\left[a_{19(\mathrm{P,T})} \pm \sqrt{a^2_{19(\mathrm{P,T})} + 4a_{20(\mathrm{P,T})}}\right] \tag{3.2}$$

where the coefficients a_{19} and a_{20} are defined by

$$a_{19\mathrm{P}} = a_{1\mathrm{P}} + a_{5\mathrm{P}} + a_{9\mathrm{P}} \tag{3.3}$$

$$a_{20\mathrm{P}} = a_{7\mathrm{P}}(a_{3\mathrm{P}} - a_{2\mathrm{P}}) + a_{8\mathrm{P}}(a_{1\mathrm{P}} - a_{3\mathrm{P}}) + a_{9\mathrm{P}}(a_{2\mathrm{P}} - a_{1\mathrm{P}}) \tag{3.4}$$

The fitting results of the purely thermal reaction immediately supply the values of the thermal rate constants as in Eqs. (3.5) and (3.6). However, when the numbers "a" and "b" are specified for a particular mechanism, the values of k_a and k_b take either of the rate constants $\vartheta_{+\mathrm{T}}$ and $\vartheta_{-\mathrm{T}}$. In other words, if the relative magnitude of the rate constants (k_a and k_b) is not known with certainty, each of them should be tested against the pair of values $\vartheta_{+\mathrm{T}}$ and $\vartheta_{-\mathrm{T}}$.

$$k_a = -\vartheta_{+\mathrm{T}} \tag{3.5}$$

$$k_b = -\vartheta_{-\mathrm{T}} \tag{3.6}$$

In the case where a mono-exponential trace is observed, the ϑ values can be attributed to the rate constant of a thermal process if there is only one thermal reaction in the mechanism. If there are two thermal processes involved in the mechanism, it is possible that the observed kinetics are wavelength-dependant and the values of k_a and k_b can be derived from mono-exponential fits as a function of λ_{obs}. (*Note*: the derived ϑ value will be equal to k_a, k_b or $k_a + k_b$.)

The few mono-exponential kinetic cases which are not solvable by the present procedure are those where only the sum of rate constants ($k_a + k_b$) is experimentally accessible, e.g., a convergent mechanism where the spectra of species A, B and C completely overlap each other and only compound A is isolable.

Step 2: Defining the Quantum Yields

The fitting of the trace generated by the photochemical reaction gives the overall reaction rates ($\vartheta_{+\mathrm{P}}$ and $\vartheta_{-\mathrm{P}}$) whose expressions incorporate combinations of the $a_{19\mathrm{P}}$ and $a_{20\mathrm{P}}$ coefficients, independent of the wavelength, as shown in Step 1 (Eqs. (3.3) and (3.4)).

The numerical values of $a_{19\mathrm{P}}$ and $a_{20\mathrm{P}}$ can be obtained by using Eqs. (3.2) and the fitting results:

$$a_{19\mathrm{P}} = \vartheta_{+\mathrm{P}} + \vartheta_{-\mathrm{P}} \tag{4.1}$$

$$a_{20\mathrm{P}} = -\vartheta_{+\mathrm{P}}\cdot\vartheta_{-\mathrm{P}} \tag{4.2}$$

As we already know the values of k_a and k_b from Step 1, we are then left with a pair of simultaneous equations involving the two unknowns ϕ_c and ϕ_d. In this situation the solution is simple, however, it can lead to several solutions if the expressions in Eqs. (3.3) and/or (3.4) are quadratic. In this case all positive roots should be retained, and each pair of roots ($\phi_c\cdot\gamma$, $\phi_d\cdot\gamma$) tested further on. This indicates that cases might exist where unique identifiability is not possible because of these different solutions.

At this stage it is important to note that the solutions obtained in the former two steps will allow all the a_1–a_9 coefficients to be numerically defined. It is also worth noting that the procedure allows the determination of all kinetic parameters (k's and specially ϕ's) before any quantitative knowledge of the spectroscopic features of compounds A, B, and C or their concentrations at the equilibrium state has been established.

Step 3: Defining the PSS Concentrations

We will use in the following another set of equations given in reference [1]. The latter formalism has been developed for a specific case where the absorbance ($M^{\lambda}_{\mathrm{P,T}}(t)$ as given by Eq. (3.1)) reflects the variation of the absorbance of both B and C isomers. We use the derived equations unchanged, however, it is worth noting that the conclusion (as can be seen below) will be applicable to any ABC($2k$,2ϕ) case (i.e. the nature of the signal analyzed does not matter).

The absorbance at the photostationary state (PSS) or at a state of thermal equilibrium (STE), which we call here $M^{\lambda}_{\mathrm{PSS,STE}}$, is given by the relationships Eqs. (5):

$$\theta^{\lambda}_{4\mathrm{P}} = -\frac{a^{\lambda}_{21\mathrm{P}}}{a_{20\mathrm{P}}} = M^{\lambda}_{\mathrm{PSS}} \tag{5.1a}$$

$$\theta^{\lambda}_{4\mathrm{T}} = -\frac{a^{\lambda}_{21\mathrm{T}}}{a_{20\mathrm{T}}} = M^{\lambda}_{\mathrm{STE}} \tag{5.1b}$$

where the coefficient a^{λ}_{21} has the following explicit form:

$$\begin{aligned} a^{\lambda}_{21(\mathrm{P,T})} = {} & \big[(a_{3(\mathrm{P,T})}\cdot a_{4(\mathrm{P,T})} - a_{1(\mathrm{P,T})}\cdot a_{6(\mathrm{P,T})})\cdot \varepsilon^{\lambda}_{\mathrm{B}} \\ & + (a_{2(\mathrm{P,T})}\cdot a_{7(\mathrm{P,T})} - a_{1(\mathrm{P,T})}\cdot a_{8(\mathrm{P,T})})\cdot \varepsilon^{\lambda}_{\mathrm{C}}\big]\cdot C_0 \end{aligned} \tag{5.2}$$

By introducing Eq. (5.2) into Eq. (5.1) we find:

$$\begin{aligned} M^{\lambda}_{\mathrm{PSS,STE}} = {} & \frac{a_{3(\mathrm{P,T})}\cdot a_{4(\mathrm{P,T})} - a_{1(\mathrm{P,T})}\cdot a_{6(\mathrm{P,T})}}{-a_{20(\mathrm{P,T})}}\cdot C_0\cdot \varepsilon^{\lambda}_{\mathrm{B}} \\ & + \frac{a_{2(\mathrm{P,T})}\cdot a_{7(\mathrm{P,T})} - a_{1(\mathrm{P,T})}\cdot a_{8(\mathrm{P,T})}}{-a_{20(\mathrm{P,T})}}\cdot C_0\cdot \varepsilon^{\lambda}_{\mathrm{C}} \end{aligned} \tag{5.3}$$

On the other hand, the absorbance at the photostationary state (or at the thermal equilibrium) is equal to the absorbance at the beginning of the thermal (as the light is switched off) or the photochemical (as the light is switched on) reaction, as defined [1] by

$$M^{\lambda}_{\mathrm{PSS,STE}} = C^{\mathrm{PSS,STE}}_{\mathrm{B}}\cdot \varepsilon^{\lambda}_{\mathrm{B}} + C^{\mathrm{PSS,STE}}_{\mathrm{C}}\cdot \varepsilon^{\lambda}_{\mathrm{C}} \tag{5.4}$$

Finally, let us compare these latter equations. It can be seen that by comparison of the terms of Eqs. (5.3) and (5.4), the formulae for the concentrations at the equilibrium states for the species B and C can be extracted as

$$C^{\mathrm{PSS,STE}}_{\mathrm{B}} = \frac{a_{3(\mathrm{P,T})}\cdot a_{4(\mathrm{P,T})} - a_{1(\mathrm{P,T})}\cdot a_{6(\mathrm{P,T})}}{-a_{20(\mathrm{P,T})}}\cdot C_0 \tag{5.5}$$

$$C^{\mathrm{PSS,STE}}_{\mathrm{C}} = \frac{a_{2(\mathrm{P,T})}\cdot a_{7(\mathrm{P,T})} - a_{1(\mathrm{P,T})}\cdot a_{8(\mathrm{P,T})}}{-a_{20(\mathrm{P,T})}}\cdot C_0 \tag{5.6}$$

Also, by using the mass balance equation (Eq. (1)), we define the last concentration of compound A:

$$C^{\mathrm{PSS,STE}}_{\mathrm{A}} = C_0 - C^{\mathrm{PSS,STE}}_{\mathrm{B}} - C^{\mathrm{PSS,STE}}_{\mathrm{C}} \tag{5.7}$$

The numerical values of the three expressions can be worked out since the values of each $a_{i\mathrm{T}}$ (Steps 1 and 2), $a_{i\mathrm{P}}$ (Step 2) and C_0 are known.

As we can see from Eqs. (5.5)–(5.7), the concentration expressions at the (photostationary or thermal) equilibrium state are exclusively dependant on the kinetic parameters, do not incorporate specific molar absorption coefficients and are not wavelength dependent. Accordingly, these represent general formulae that are valid for all sequences independently of the nature of the signal that has been analyzed (containing one, two or three cumulative absorbances).

Furthermore, because these results are true as well for the ABC($6k$,6ϕ) general model, a more important and general definition emerges with relation to the equilibrium concentration ratio (K_{eq}). Depending on the specific dynamics involved, the relationship (Eq. (5.8)) is applicable to purely thermal, purely photochemical or combined thermal/photochemical reactions in order to define the concentration ratio at an equilibrium state.

$$K^{\mathrm{PSS,STE}}_{\mathrm{eq}} = \frac{C^{\mathrm{PSS,STE}}_{\mathrm{B}}}{C^{\mathrm{PSS,STE}}_{\mathrm{C}}} = \frac{a_{3(\mathrm{P,T})}\cdot a_{4(\mathrm{P,T})} - a_{1(\mathrm{P,T})}\cdot a_{6(\mathrm{P,T})}}{a_{2(\mathrm{P,T})}\cdot a_{7(\mathrm{P,T})} - a_{1(\mathrm{P,T})}\cdot a_{8(\mathrm{P,T})}} \tag{5.8}$$

An immediate consequence of the definition of the concentrations in analytical forms (Eqs. (5.5)–(5.7)) is found in solving the identifiability of those ABC systems possessing an equilibrium state and whose kinetic parameters (a_i coefficients) are known (see Step 4).

Step 4: Defining the Molar Absorption Coefficients

In order to quantify the spectroscopic features of the species, the final step of the procedure brings in the use of the initial velocity equations relating to the photochemical as well as the thermal reactions. These quantities have the following forms [1]:

$$\begin{aligned} m^{\lambda}_{0(\mathrm{P,T})} = {} & \big(a_{1(\mathrm{P,T})}\cdot \varepsilon^{\lambda}_{\mathrm{A}} + a_{4(\mathrm{P,T})}\cdot \varepsilon^{\lambda}_{\mathrm{B}} + a_{7(\mathrm{P,T})}\cdot \varepsilon^{\lambda}_{\mathrm{C}}\big) \\ & \cdot C^{0,\mathrm{PSS,STE}}_{\mathrm{A}} + \big(a_{2(\mathrm{P,T})}\cdot \varepsilon^{\lambda}_{\mathrm{A}} + a_{5(\mathrm{P,T})}\cdot \varepsilon^{\lambda}_{\mathrm{B}} \\ & + a_{8(\mathrm{P,T})}\cdot \varepsilon^{\lambda}_{\mathrm{C}}\big)\cdot C^{0,\mathrm{PSS,STE}}_{\mathrm{B}} + \big(a_{3(\mathrm{P,T})}\cdot \varepsilon^{\lambda}_{\mathrm{A}} \\ & + a_{6(\mathrm{P,T})}\cdot \varepsilon^{\lambda}_{\mathrm{B}} + a_{9(\mathrm{P,T})}\cdot \varepsilon^{\lambda}_{\mathrm{C}}\big)\cdot C^{0,\mathrm{PSS,STE}}_{\mathrm{C}} \end{aligned} \tag{6.1}$$

where C_X^0 (or C_X^{STE}) and C_X^{PSS}, expressing the concentrations (X = A, B, or C) at different specific times, are correlated to the labels "P" and "T," respectively.

The numerical values of m_{0P} and m_{0T} are obtained graphically from the treatment of the experimental kinetic traces (or available from the fitting in the cases where Eq. (3.1) is applied). We then have two equations to identify the two unknowns ε_B^λ and ε_C^λ. However, for the cases in which no information on the spectroscopic properties of the species (A, B, and C) involved are available (including those situations where the three species are characterized by very similar absorption spectral shapes), we would require one more equation to obtain the three unknown extinction coefficients. At this stage, we make use of the equations for the initial absorbance before any reaction takes place (M_0), at the photostationary state (M_{PSS}) and at the equilibrium (completion) of the thermal reaction (M_{STE}). These can be written in a general form as shown in Eq. (6.2), but each case will have a specific expression according to the occurrence of the concentrations, molar absorption coefficients and/or the number of species responsible for the signal measured.

$$M_\alpha^\lambda = \varepsilon_A^\lambda \cdot C_A^\alpha + \varepsilon_B^\lambda \cdot C_B^\alpha + \varepsilon_C^\lambda \cdot C_C^\alpha \tag{6.2}$$

where $\alpha = 0$, PSS or STE.

Therefore, in all cases, Eq. (6.2) will generate extra equations (two or more) that will allow us to complete the parameter-defining procedure. Any spare equations (not used in Step 4) can be employed to validate the whole parameter set.

A by-product of this procedure is that we can establish a definition of the colorability of photochromic ABC systems such as chromenes, where the photochemical reaction starts with a single, thermally stable species. In the case of AB(1ϕ) systems, the colorability has been defined as the product of quantum yield and the extinction coefficient of the B (colored) species. This is also applicable to AB($1k$,1ϕ) systems if the measurements are carried out so as to cancel out the thermal process; for illustration, many spiropyrans under flash photolysis conditions have been used as application examples [7].

For the systems studied here, Eq. (6.1) reduces to an expression made up exclusively by extinction coefficients and quantum yields of the colored species times the initial concentration. Accordingly, the expression for the colorability (COL) for these cases can be derived from the initial velocity of the photochemical reaction, on the basis of Eq. (6.1). The colorability is given by Eq. (6.3), which is defined specifically at the observation wavelength but is independent of the medium temperature, the concentration of the starting material, the spectral composition of the signal (e.g. Eq. (6.3) is applicable whether one, two or all three species contribute to the spectrum at λ_{obs}), the absorbance at the irradiation wavelength (that of the isosbestic point) and the incident light intensity. It should also provide the same results for a system under flash or continuous irradiation conditions.

$$\mathrm{COL} = \frac{m_{0P}^\lambda}{C_A^0 \cdot \gamma} = -(\phi_4 + \phi_{12}) \cdot \varepsilon_A^\lambda + \phi_4 \cdot \varepsilon_B^\lambda + \phi_{12} \cdot \varepsilon_C^\lambda \tag{6.3}$$

Since the quantities m_{0P}^λ, γ and $C_A^0 = C_0$ involved in Eq. (6.3) are all available experimentally, the colorability may be calculated even though the mechanism exceeds the ABC($2k$,2ϕ) model, or is unknown altogether (provided that the conditions set above are valid). This represents an efficient and an easily evaluated criterion to compare with the colorability of analogous systems; e.g., for different (naphtho or spiro) pyran derivatives or between a set of identical experiments carried out in different media. Finally, it is worth noting that Eq. (6.3) reduces to the exact definition for the colorability of an AB system as the one already established in the literature [7].

Algorithm of the Procedure

In the following we provide a flowchart of the different steps of the procedure.

1. Write down the sequence that represents the photochemical/thermal ABC($2k$,2ϕ) or ABC($2k$,1ϕ) dynamics under study.
2. Identify the initial concentration values (Eq. (1): total C_0 and individual C_A^0, C_B^0 and C_C^0).
3. Write down the a_{1P}–a_{9P} coefficients for the specified sequence (Eqs. (2)).
4. Fit the experimental kinetic traces to the appropriate bi-exponential equation (Eq. (3.1)).
5. Calculate the rate constants for the thermal reaction(s) (k_a, k_b) using Eqs. (3.5) and (3.6).
6. Write down the equations for a_{19P} and a_{20P} (Eqs. (3.3) and (3.4)) and calculate their values (Eqs. (4)).
7. Calculate the quantum yields ($\phi_c \cdot \gamma$, $\phi_d \cdot \gamma$) by solving Eqs. (3.3) and (3.4).
8. Calculate the numerical values of the a_{1P}–a_{9P} and a_{1T}–a_{9T} coefficients.
9. Define the species concentrations at the photostationary state (C_A^{PSS}, C_B^{PSS} and C_C^{PSS}) and at the state of thermal equilibrium (C_A^{STE}, C_B^{STE} and C_C^{STE}) by applying Eqs. (5.5)–(5.7).

10. Write down the expressions of the initial quantities M_{0P}^{λ}, M_{PSS}^{λ}, M_{STE}^{λ}, m_{0P}^{λ} and m_{0T}^{λ} according to Eqs. (6.1) and (6.2), and calculate their numerical values from the experimental traces.
11. Define the molar absorption coefficients ($\varepsilon_{A}^{\lambda}$, $\varepsilon_{B}^{\lambda}$ and $\varepsilon_{C}^{\lambda}$) by solving the appropriate system of equations from point 10.
12. Retrieve the complete individual spectra of the (three) compounds by calculating the molar absorption coefficients at different wavelengths using each time the operations described in points 10 and 11.

APPLICATION EXAMPLE: NAPHTHOPYRAN KINETICS

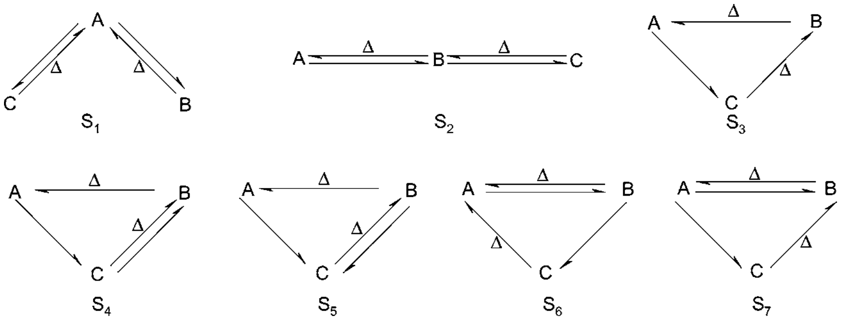
The dynamics of 3,3-diaryl-3*H*-naphtho[2,1-*b*]pyrans (NPY) are known to obey a kinetic sequence derived from the general ABC($4k$,6ϕ) frame model (two rate constants have been deleted as the compounds are not thermochromic at 14°C). However, their dynamics have not been elucidated with certainty. In our previous paper [2], we have shown that even for preconceived mechanisms the difficult issue of identifiability is encountered in elucidating the parameter set. This means that it is possible to find a number of different solutions for the kinetic and spectroscopic parameter set, with in each case, the model exactly reproducing the experimental traces.

In the light of our interest in NPY dynamics, we apply the procedure developed in the present work in order to solve the identifiability problem for all possible ABC($2k$,2ϕ) NPY sequences. Through this investigation, we will be able to demonstrate whether or not the kinetics of the NPY system can be represented by an ABC($2k$,2ϕ) mechanism; a result that has not been demonstrated to date.

Inside the general ABC($2k$,2ϕ) model, seven possible options including divergent, consecutive and cyclic mechanisms can be found to describe the NPY kinetics (Scheme 2). Among this series there is a single sequence which incorporates only three reaction steps (S_3 is an ABC($2k$,1ϕ) system).

Experimental kinetic traces of the photochemical and thermal reactions of 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran have been recorded in 5.87×10^{-5} M ethyl acetate solutions at 14°C (Fig. 1). The same experimental set-up and reaction conditions as reference [2] have been used here except when otherwise specified. The irradiation wavelength corresponds to the isosbestic point situated at $\lambda_{irr} = 358$ nm. The observation wavelength was that of the maximum absorption of the photoisomers ($\lambda_{obs} = 423$ nm). The fitting has been performed using Eq. (3.2) because the analytical signal recorded in the visible region is due to the appearance of the isomers B and C when the initial species A is irradiated. The curves are fitted with high accuracy with the corresponding parameter values given in Table I.

We have applied the step-by-step procedure described here to each of the sequences S_1–S_7 and obtained their kinetic and spectroscopic parameters. The results showed that except for three mechanisms (S_1, S_5 and S_7), in all other cases at least one of the determined parameters has a negative value. According to our procedure and the outcome of its application, only positive parameter values are expected to be found. This means that the possible reaction mechanisms (S_2–S_4 and S_6) showing such features cannot represent the NPY dynamics and must be ruled out. Hence, our method can provide a useful means to investigate the distinguishability of ABC($2k$,2ϕ) mechanisms. The three remaining candidates (divergent S_1 and cyclic S_5, S_7) have been analyzed according to the procedure using the data of Table I. We have employed the resulting values of a_{19P} and a_{20P} ($= -0.01444$ and -1.77331×10^{-4}, respectively) to define the quantum yields, and in order to extract the molar absorption coefficients the initial



Scheme 2 NPY sequences (S_1–S_7) obeying the ABC($2k$,2ϕ) and ABC($2k$,1ϕ) kinetic models (here the symbol "Δ" indicates the thermal process).

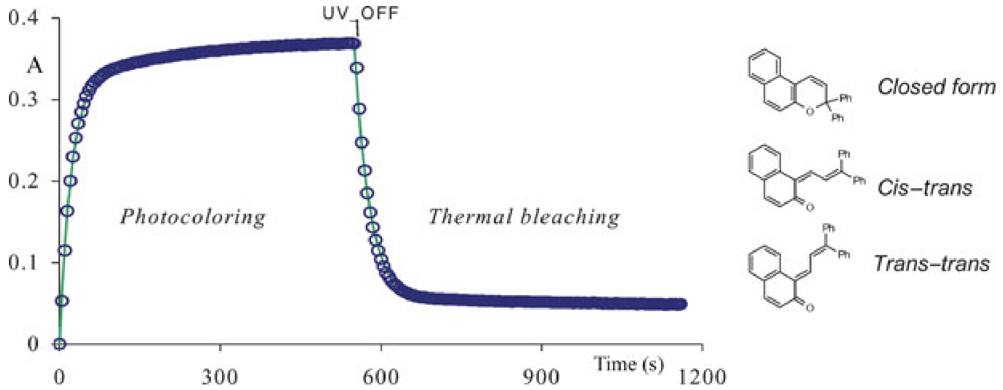


Figure 1 Experimental (circles) and fitting (line) kinetic traces of the coloring and thermal bleaching of NPY (structures aside) in ethyl acetate ($\lambda_{\rm irr} = 357$ nm, $\lambda_{\rm obs} = 423$ nm, $C_0 = 5.87 \times 10^{-5}$ mol L^{-1}, $T = 14°$C).

m_{0P} and M_{0T} (Eqs. (7)) have been used. The resulting parameter sets are reported in Table II.

$$m_{0P}^{423} = \left(\phi_{AB} \cdot \varepsilon_B^{423} + \phi_{AC} \cdot \varepsilon_C^{423}\right) \cdot \gamma \cdot C_0 \quad (7.1)$$

$$M_{0T}^{423} = \varepsilon_B^{423} \cdot C_B^{PSS} + \varepsilon_C^{423} \cdot C_C^{PSS} \quad (7.2)$$

The similarity of the results obtained for S_1 and S_7 (Table II) comes from a close correspondence between the series of expressions defining the a_1–a_9 coefficients. This feature underlines the distinguishability problem in relation to such kinetics. However, in the specific case of NPY kinetics, we consider that it is possible to rule out two of the three remaining possible mechanisms. First, even if we had not attributed molecular structures to isomers B and C, it is rather unlikely that both the *trans–trans* and the *cis–trans* open form isomers react identically as is suggested by S_1. Specifically, that their thermal routes exclusively lead to the closed form. If this is acceptable for the *trans–cis* isomer, it seems very improbable for its *trans–trans* homologue. Since the latter needs to overcome two energy barriers in order to revert to the closed form and since one of these barriers most probably corresponds to the isomerization of the *trans–trans* species into the *cis–trans* isomer, we believe that it is not realistic to consider a mechanism that contains the *cis–trans* → NPY reaction without simultaneously allowing the *trans–trans* → *cis–trans* reaction step. These criteria are not contained within the divergent sequence (S_1), and hence we feel it should be excluded from consideration. Mechanism S_5 is excluded on the basis that species B cannot be represented by the *trans–trans* isomer because of the unlikely occurrence of such thermal reaction (*trans–trans* → NPY, as discussed for S_1 above) and hence S_5 would indicate that the photoreactions of both the NPY and the *cis–trans* species exclusively yield the *trans–trans* species. This situation is physically improbable for that it supposes the system reacting through strained photochemical pathways (NPY → *trans–trans* ← *cis–trans*) while omitting much simpler ones (notably NPY → *cis–trans* and its reverse transformation).

On this basis, S_7 seems the only mechanism that plausibly fits NPY kinetics if it is assumed to be an ABC($2k$,2ϕ) system. The attribution of B and C structures for this sequence is carried out in agreement with the latter discussion, i.e. the *cis–trans* isomer is the intermediate species (B) in the thermal process (C → B → NPY).

The kinetic behavior of NPY as predicted by S_7 suggests that only the closed form is photochemically

Table I Fitting Parameters Respectively for the Photocoloring and Thermal Bleaching Kinetic Traces of NPY in Ethyl Acetate

	Parameter					
Reaction	$m_{0(T,P)}(s^{-1})$	$M_{0(T,P)}$	$\theta_{4(T,P)}$[a]	$\nu_{+(T,P)}(s^{-1})$	$\nu_{-(T,P)}(s^{-1})$	r^2[b]
Photochemical	0.01518	0	0.3756	−0.04606	−0.00385	0.999
Thermal	−0.01109	0.3690	0	−0.03528	−0.00019	0.998

[a] These constants, indicating the values of the absorbances at $t = \infty$, are obtained by the fitting without imposing any constraints on their values.

[b] Squared correlation coefficient values obtained on the experimental vs. calculated absorbance graphs.

Table II Determined Parameter Values[a] Characterizing the Uniquely Identifiable Solutions for Mechanisms S$_1$, S$_5$ and S$_7$

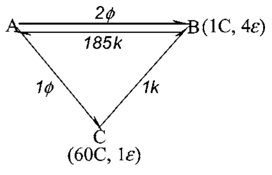
	$\phi_i \cdot \gamma\,(\mathrm{s}^{-1})$	$\phi_i \cdot \gamma\,(\mathrm{s}^{-1})$	$C_\mathrm{A}^\mathrm{PSS}(\mathrm{mol\,L^{-1}})$	$C_\mathrm{B}^\mathrm{PSS}(\mathrm{mol\,L^{-1}})$	$C_\mathrm{C}^\mathrm{PSS}\,(\mathrm{mol\,L^{-1}})$	$\varepsilon_\mathrm{B}^\lambda$ (mol^{-1} L cm^{-1})	$\varepsilon_\mathrm{C}^\lambda$ (mol^{-1} L cm^{-1})
S$_1$	$\phi_\mathrm{AB} \cdot \gamma$ 9.65×10^{-3}	$\phi_\mathrm{AC} \cdot \gamma$ 4.78×10^{-3}	2.219×10^{-6}	6.072×10^{-7}	5.587×10^{-5}	23637	6347
S$_5$	$\phi_\mathrm{BC} \cdot \gamma$ 1.07×10^{-2}	$\phi_\mathrm{AC} \cdot \gamma$ 3.69×10^{-3}	2.219×10^{-6}	2.322×10^{-7}	5.625×10^{-5}	70050	6271
S$_7$	$\phi_\mathrm{AB} \cdot \gamma$ 9.68×10^{-3}	$\phi_\mathrm{AC} \cdot \gamma$ 4.76×10^{-3}	2.219×10^{-6}	9.082×10^{-7}	5.557×10^{-5}	23638	6254

[a] The thermal rate constants for these mechanisms are k_BA (S$_1$, S$_5$ and S$_7$) = 0.03528 s^{-1} and k_CB (S$_5$ and S$_7$) = k_CA (S$_1$) = 0.00019 s^{-1}.

active, and forms species B twice as efficiently as species C (Table II). The thermal back-recyclization reaction of B (characterized by k_BA) is much faster than the isomerization of C into B (rate constant k_CB). As a consequence, the concentration of compound B at the photostationary state is around 60 times less than that of compound C at the photostationary state (Scheme 3). On the basis of the latter figures, the contribution of C to the observed spectrum of the mixture (at the PSS) is expected to be much more important than that of B because its molar absorption coefficient is estimated to be only four times less than that of B (which does not compensate for the difference in the concentrations) (Fig. 2).

Although the results given in Table II seem satisfactory, it is however compulsory that before S$_7$ is definitely accepted as the true mechanism, all equations characterizing both the photochemical and the thermal reactions are checked for consistency. For example, we can consider Eqs. (8), which represents the initial velocity and the pre-exponential terms of the fading process. Their values can be retrieved from the fitting results (Table I).

$$m_{0\mathrm{T}}^{423} = -k_2 \cdot C_\mathrm{B}^\mathrm{PSS} \cdot \varepsilon_\mathrm{B}^{423} + k_5 \cdot \left(\varepsilon_\mathrm{B}^{423} - \varepsilon_\mathrm{C}^{423}\right) \cdot C_\mathrm{C}^\mathrm{PSS} \tag{8.1}$$



S$_7$

Scheme 3 Predicted kinetic parameters of the NPY ABC($2k$,2ϕ) sequence (S$_7$).

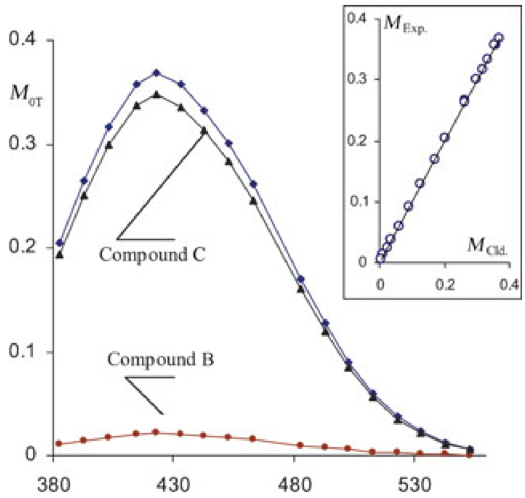


Figure 2 Calculated spectra of individual species B (○) and C (△) for mechanism S$_7$ and the experimental spectrum of their mixture (□) in the visible region. *Inset*: correlation line ($r^2 = 0.99$) between calculated and experimental data of the mixture.

$$\theta_{1\mathrm{T}}^{423} = -\frac{m_{0\mathrm{T}}^{423} - M_{0\mathrm{T}}^{423} \cdot \vartheta_{-\mathrm{T}}}{\vartheta_{-\mathrm{T}} - \vartheta_{+\mathrm{T}}} \tag{8.2}$$

$$\theta_{2\mathrm{T}}^{423} = \frac{m_{0\mathrm{T}}^{423} - M_{0\mathrm{T}}^{423} \cdot \vartheta_{+\mathrm{T}}}{\vartheta_{-\mathrm{T}} - \vartheta_{+\mathrm{T}}} \tag{8.3}$$

It becomes apparent from the calculated values of these expressions, by exclusively using the data from Table II, that these do not correspond to those obtained from the fitting of the traces. This means also that depending on the pair of equations we use to fulfill Step 4 of the procedure—here we can pick any two from the three Eqs. (7.1), (7.2) and (8.1) available—we find a different set of ε values. It is worth noting the power of our procedure specifically because it affords these auto-checking options. This should be possible for any situation (this might generally be true owing to the fact that Eqs. (6) in Step 4 generates more equations than the two needed for the determination of the molar absorption coefficients). In the case of our $3H$-naphtho[2,1-*b*]pyran derivative, these results prove incontestably that its kinetics does not obey any of the sequences presented in Scheme 2 and, therefore, it should be described by a higher level mechanism than ABC($2k$,2ϕ). This conclusion is consistent with the fact that there is no objective reason to rule out the photochemical reactivity of the NPY photoisomers as has been proven for its homologue $2H$-naphthopyran structure [10] and some spiro-naphthopyrans [7].

However, some information about the mechanism may be obtained from a close analysis of the experimental data. Indeed, when the initial velocities ($m_{0\mathrm{T}}^{\lambda}$ and $m_{0\mathrm{P}}^{\lambda}$) are plotted against the absorbance of the mixture ($M_{0\mathrm{T}}^{\lambda}$) at the PSS for each wavelength (380–580 nm) as obtained from the fitting of the traces, straight lines are obtained (Fig. 3) with intercepts equal to zero. Although, the actual mechanism taking place in the dynamics of NPY is unknown (and we do not assume one), the experimental data in Fig. 3 collected at the PSS are strictly dependant on the variation of the extinction coefficients of B and C (which are also unknown) as the real kinetic parameters and concentrations are constant (at the PSS). On the other hand, we observe that for any possible thermal sequence (which can involve between two and four reaction steps) [2], the initial velocity should have the form of Eq. (9). Also, the absorbance at the PSS of the mixture (Eq. (7.2)) and the initial velocity of the photochemical reaction (Eq. (7.1)) can be rearranged to the same algebraic form.

$$Q^{\lambda} = \alpha_i \cdot \varepsilon_{\mathrm{B}}^{\lambda} + \beta_i \cdot \varepsilon_{\mathrm{C}}^{\lambda} \tag{9}$$

where Q is the quantity considered ($m_{0\mathrm{T}}$, $m_{0\mathrm{P}}$ or $M_{0\mathrm{T}}$), α_i and β_i are constants depending on rate constants, photochemical yields and concentrations at the PSS.

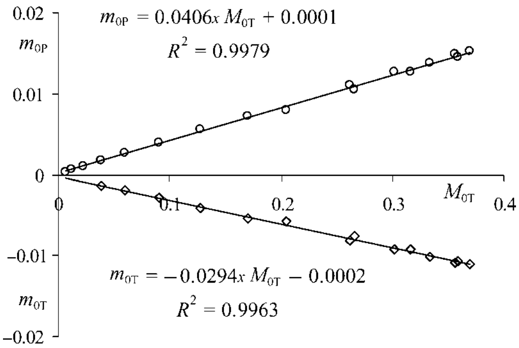


Figure 3 Linear correlation between initial velocities of the thermal ($m_{0\mathrm{T}}^{\lambda}$) and photochemical ($m_{0\mathrm{P}}^{\lambda}$) reactions with the absorbance ($M_{0\mathrm{T}}^{\lambda}$) of the medium at the PSS (or the beginning of the thermal reaction). Wavelength range 380–580 nm.

Because the ratios of any two of these three quantities ($m_{0\mathrm{T}}^{\lambda}$, $m_{0\mathrm{P}}^{\lambda}$ and $M_{0\mathrm{T}}^{\lambda}$) are constant for all wavelengths (see correlation equations in Fig. 3), we can demonstrate (see Appendix) that within the wavelength range considered the spectra of the NPY photoisomers B and C are characterized by an identical shape.

These results are in agreement with the transient and permanent spectra obtained from nanosecond experiments on the *trans–trans* isomer photoreaction of a $2H$-NPY analogue [10].

CONCLUSION

A new procedure to solve analytically the kinetics of ABC($2k$,2ϕ) systems has been presented here in four progressive steps. It is valid for any photochemical system independent of the signal composition or the trends of the intensity variation, provided that its kinetic traces exhibit a bi-exponential trend. For the determination of the unknowns (at least eight), it is only necessary to know the initial total concentration. The output will encompass all the kinetic parameters of the reactions as well as the spectroscopic details of the three species (i.e. nine parameters). Henceforward, the method provides an easy way to retrieve the individual spectra of the transient structures that may be involved in the dynamics. It affords options to auto-check the results found without a need for further external data. It solves finally the identifiability problem for the whole class of ABC($2k$,2ϕ) systems. In the course of establishing this procedure on the basis of our previous formalism, we have produced two general expressions for the colorability of ABC systems and for the concentration equilibrium ratio of the species involved in the reaction (K_{eq}) as a function of the kinetic parameters, which is useful for any ABC($6k$,6ϕ) system.

We have shown an example of the application of the procedure by considering NPY kinetics. For this particular compound it was possible to rule out many possible mechanisms because some of the parameter values generated by applying our method were found to be negative. Furthermore, it was then argued that when the procedure was fully conducted, we reached the conclusion that in the NPY kinetics there are certainly more photochemical processes than the two considered in the ABC($2k$,2ϕ) sequence. We address these issues in the next paper in this series.

APPENDIX

For any single mechanism, we can write the expressions of $m_{0\mathrm{T}}$, $m_{0\mathrm{P}}$ and $M_{0\mathrm{T}}$ in the form given by Eq. (9), which is valid for each single wavelength of the considered range. The ratios of any two of these quantities at any wavelength, denoted here as Q_1 and Q_2, are given by Eq. (A1). The ratios spanning over all wavelengths are equal to a single experimentally defined constant (Γ) as depicted by the straight lines in Fig. 3. The α_i and β_i are constants as discussed above.

$$\forall \varepsilon_{\mathrm{B}}^{\lambda} \text{ and } \varepsilon_{\mathrm{C}}^{\lambda} \Rightarrow \frac{Q_1^{\lambda}}{Q_2^{\lambda}} = \frac{\alpha_1 \cdot \varepsilon_{\mathrm{B}}^{\lambda} + \beta_1 \cdot \varepsilon_{\mathrm{C}}^{\lambda}}{\alpha_2 \cdot \varepsilon_{\mathrm{B}}^{\lambda} + \beta_2 \cdot \varepsilon_{\mathrm{C}}^{\lambda}} = \Gamma \quad \text{(A1)}$$

This expression can be rearranged as follows:

$$\Gamma = \frac{\alpha_1 + \beta_1 \cdot (\varepsilon_{\mathrm{C}}^{\lambda}/\varepsilon_{\mathrm{B}}^{\lambda})}{\alpha_2 + \beta_2 \cdot (\varepsilon_{\mathrm{C}}^{\lambda}/\varepsilon_{\mathrm{B}}^{\lambda})} \quad \text{(A2)}$$

from which the formula of the extinction coefficients ratio is defined as:

$$\forall \lambda;\ 380\,\mathrm{nm} < \lambda < 580\,\mathrm{nm} \Rightarrow \frac{\varepsilon_{\mathrm{C}}^{\lambda}}{\varepsilon_{\mathrm{B}}^{\lambda}} = \frac{\Gamma \cdot \alpha_2 - \alpha_1}{\beta_1 - \Gamma \cdot \beta_2} = n \quad \text{(A3)}$$

Since all the coefficients in the right-hand side term are constants, the ratio is a constant "n" for all wavelengths. This means that the spectra of isomers B and C have the same shape.

The above consideration is true for all the equations of $m_{0\mathrm{P}}$ irrespective of the mechanism. Indeed, the latter quantity is defined depending on the photochemical reactivity of the starting material (NPY); it can involve either one process (ϕ_4 or $\phi_{12} \neq 0$) or two processes (ϕ_4 and $\phi_{12} \neq 0$) as given by Eq. (7.1).

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