

The kinetic model for AB(1 ϕ) systems A closed-form integration of the differential equation with a variable photokinetic factor

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Abstract

A kinetic law, the log–exp model, that describes the evolution of a unimolecular photochemical reaction, AB(1 ϕ), has been realised for the first time through a closed-form integration of the differential equation that involves a time-dependent photokinetic factor. As a consequence, a novel analytical formula for the efficiency of AB(1 ϕ) photoreactions has been established. The theoretical log–exp model has been successfully tested against numerical integration data for simulated kinetics. It has been applied to the direct determination of the absolute values of the quantum yields, at different visible irradiation wavelengths, for the photoisomerization of a diarylethene derivative in an organic medium.

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1. Introduction

Despite the importance of theoretical kinetic models in the field of reaction dynamics, the differential equation describing the progress of a unimolecular photoreaction involving the transformation of an initial species A into a product B (vide infra Eq. (1a)) has thus far represented a challenge to kineticists and has remained unsolved [1–13]. In fact, a lack of analytical kinetic laws is noticeable for all basic first-order photochemical AB systems, irrespective of the number of reaction steps involved in the bimolecular process (at most equal to four: two pairs of opposing photochemical and thermal reactions) [1–12]; the only exceptions are those reactions performed under isosbestic irradiation [13,14].

The difficulty in achieving a closed-form integration of these differential equations stems from the time-variation of the photokinetic factor (vide infra Eq. (1c)), which is variable because of its explicit dependence on the total absorbance of the medium at the irradiation wavelength (the latter being different from that of

the isosbestic point) [1–6]. Because no integration procedures exist to readily solve the mathematical form of the resulting differential equation (i.e. Eq. (1a)), dealing with such kinetics has so far meant resorting to either approximation methods or implementing a numerical integration [1–10]. Tomlinson et al. [15] have proposed the first parametric model for reversible photodimerisation in a rigid matrix that expresses the intensity of the transmitted light (I_{tr}) as a function of time. In this approach, an estimate of the *initial* quantum efficiency can only be obtained if the initial part of the latter curve is reasonably straight and a reliable estimation of the light saturation-intensity value (I_s , the model's parameter) is obtained by extrapolating the curve $I_{tr} = f(t)$. Other approaches have been proposed by Brauer et al. for actinometry [16–18], among these an empirical model [16], formally similar to the preceding one [15], where absorbances replaced light intensities. Equally, this approximation can only be considered if the logarithmic coefficient involving the variable absorbance of the reaction medium is linear with irradiation time (which is essentially a similar condition to that imposed by the preceding method [15]).

More recently, Bossi et al. [19] have used a simplified model in which the determination of the quantum yield values for fulgide photoisomerization reactions (including the

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photobleaching where the coloured isomer (E) is reverted to the closed-form (C) under visible irradiation) was carried out under the provision that the total absorbance of the reaction medium at the irradiation wavelength was kept low (i.e. less than 0.05). In these circumstances, the photokinetic factor of the fundamental equation could be approximated to a constant and the kinetics of the studied unimolecular photoreaction could be described by a first-order homogeneous differential equation. The latter differential equation is then readily solved by the variable separation method.

Similarly, it is noticeable that a monoexponential model has been used to fit the kinetic trace corresponding to the photobleaching (a one step recyclisation reaction) of a coloured and thermally stable indeno-fused naphthopyran (here the trace has been obtained by using an irradiation with visible light ($\lambda_{\text{irr}} > 420$ nm); λ_{irr} is situated near the maximum absorption of the isomer) [20].

It is a fact, however, that these and similar approaches lack the absolute theoretical rigour to yield the kinetic law for the unimolecular photoreaction kinetics and/or a useful analytical definition for its quantum yield [1–34].

In this study, we present for the first time the kinetic law for the photochemical transformation of a single absorbing species into its photoproduct. A definition for the quantum yield has also been established. The relationship is obtained through a closed-form integration of the differential equation. It has been tested against a theoretical data set and applied to the photochemical cycloreversion of a diarylethene derivative.

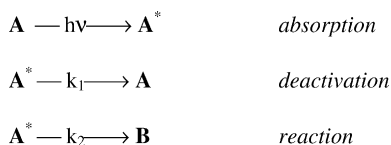
2. The log–exp kinetic model

The fundamental processes taking place in a photochemical transformation of species A into species B can be considered to involve three steps (Scheme 1). The excited state molecules (A^*) of species A are produced after the absorption of the excitation photons. The A^* molecules undergo processes by which they either deactivate to the ground state (A) or generate the photoproduct B. The photochemical quantum yield of the transformation is then given by the ratio $\phi = k_2(k_1 + k_2)^{-1}$ [5].

In a photochemical reactor, steadily and continuously stirred and where the concentration in the excited state is supposed negligible, the kinetic equation for the AB(1ϕ) reaction is expressed by [1,2]:

$$\frac{dC_A(t)}{dt} = -\phi_{\text{AB}}^{\lambda_{\text{irr}}} I_0^{\lambda_{\text{irr}}} \varepsilon_A^{\lambda_{\text{irr}}} C_A(t) l_{\text{irr}} \frac{1 - 10^{-M_{\text{Tot}}^{\lambda_{\text{irr}}}(t)}}{M_{\text{Tot}}^{\lambda_{\text{irr}}}(t)} \quad (1a)$$

where C_A represents the concentration of species A in the medium at any reaction time, l_{irr} the optical path length of the excitation light, $\phi_{\text{AB}}^{\lambda_{\text{irr}}}$ the quantum yield of the photochemical



Scheme 1.

reaction, $I_0^{\lambda_{\text{irr}}}$ the incident light intensity received by the sample, $\varepsilon_A^{\lambda_{\text{irr}}}$ the extinction coefficient of species A and $M_{\text{Tot}}^{\lambda_{\text{irr}}}$ is the total absorbance of the reaction medium expressed by:

$$M_{\text{Tot}}^{\lambda_{\text{irr}}}(t) = \varepsilon_A^{\lambda_{\text{irr}}} C_A(t) l_{\text{irr}} + \varepsilon_B^{\lambda_{\text{irr}}} C_B(t) l_{\text{irr}} \quad (1b)$$

In Eq. (1a), the analytical formula of the photokinetic factor,

$$F_{\text{Tot}}^{\lambda_{\text{irr}}}(t) = \frac{1 - 10^{-M_{\text{Tot}}^{\lambda_{\text{irr}}}(t)}}{M_{\text{Tot}}^{\lambda_{\text{irr}}}(t)} \quad (1c)$$

is a time-dependent function. In this condition, there is no published analytical mathematical procedure which delivers the true integral of Eq. (1a) [1–34], and hence so far, the kinetic law of such systems has not been reported in the literature.

For a unimolecular photoreaction, where only species A is exposed to the monochromatic beam during the irradiation, the equation of the total absorbance is expressed by a single term

$$M_{\text{Tot}}^{\lambda_{\text{irr}}}(t) = M_A^{\lambda_{\text{irr}}}(t) = \varepsilon_A^{\lambda_{\text{irr}}} C_A(t) l_{\text{irr}} \quad (2a)$$

Consequently, the following differential equation is obtained

$$\frac{dC_A(t)}{dt} = -\phi_{\text{AB}}^{\lambda_{\text{irr}}} I_0^{\lambda_{\text{irr}}} (1 - 10^{-M_A^{\lambda_{\text{irr}}}(t)}) \quad (2b)$$

If we take into account the previous provisions and separate the variables of the equation, we find

$$\frac{dM_A^{\lambda_{\text{irr}}}(t)}{1 - 10^{-M_A^{\lambda_{\text{irr}}}(t)}} = (-\phi_{\text{AB}}^{\lambda_{\text{irr}}} I_0^{\lambda_{\text{irr}}} l_{\text{irr}} \varepsilon_A^{\lambda_{\text{irr}}}) dt \quad (2c)$$

In order to achieve the integration of the left-hand side term of Eq. (2c) it is necessary to make use of a change of variable, e.g. $d(10^{M_A^{\lambda_{\text{irr}}}(t)}) = (\ln(10))10^{M_A^{\lambda_{\text{irr}}}(t)} dM_A^{\lambda_{\text{irr}}}(t)$, where \ln is the Neperian logarithm.

Hence, integration of Eq. (2c) yields

$$\begin{aligned} \int \frac{d(M_A^{\lambda_{\text{irr}}}(t))}{1 - 10^{-M_A^{\lambda_{\text{irr}}}(t)}} &= \frac{1}{\ln 10} \int \frac{d(10^{M_A^{\lambda_{\text{irr}}}(t)})}{10^{M_A^{\lambda_{\text{irr}}}(t)} - 1} \\ &= - \int [\phi_{\text{AB}}^{\lambda_{\text{irr}}} I_0^{\lambda_{\text{irr}}} l_{\text{irr}} \varepsilon_A^{\lambda_{\text{irr}}}] dt \end{aligned} \quad (3a)$$

i.e.

$$\frac{1}{\ln(10)} \ln \left(\frac{10^{M_A^{\lambda_{\text{irr}}}(t)} - 1}{10^{M_A^{\lambda_{\text{irr}}}(0)} - 1} \right) = -\phi_{\text{AB}}^{\lambda_{\text{irr}}} I_0^{\lambda_{\text{irr}}} l_{\text{irr}} \varepsilon_A^{\lambda_{\text{irr}}} t \quad (3b)$$

Reformulating Eq. (3b) yields the general expression of the kinetic law,

$$M_A^{\lambda_{\text{irr}}}(t) = \log[1 + (10^{M_A^{\lambda_{\text{irr}}}(0)} - 1) e^{-(\phi_{\text{AB}}^{\lambda_{\text{irr}}} \varepsilon_A^{\lambda_{\text{irr}}} l_{\text{irr}} I_0^{\lambda_{\text{irr}}} \ln(10)) \cdot t}] \quad (3c)$$

where \log represents the base 10 logarithm.

Also, from this relationship we can define new expressions for the following quantities:

(i) the quantum yield of a unimolecular photoreaction,

$$\phi_{\text{AB}}^{\lambda_{\text{irr}}} = \frac{\ln[(10^{M_A^{\lambda_{\text{irr}}}(0)} - 1)/(10^{M_A^{\lambda_{\text{irr}}}(t)} - 1)]}{\ln(10) \varepsilon_A^{\lambda_{\text{irr}}} l_{\text{irr}} I_0^{\lambda_{\text{irr}}} t} \quad (4a)$$

(ii) the reaction half-life time ($t_{1/2}$),

$$t_{1/2} = \frac{1}{a_{AB}} \ln(10^{M_A^{\lambda_{irr}}(0)/2} + 1) \quad (4b)$$

where the coefficient $a_{AB} = \phi_{AB}^{\lambda_{irr}} \varepsilon_A^{\lambda_{irr}} l_{irr} I_0^{\lambda_{irr}} \ln(10)$ represents the overall photoreaction rate; and,

(iii) the initial velocity of the photochemical reaction,

$$m_A^{\lambda_{irr}}(0) = \left[\frac{dM_A^{\lambda_{irr}}(t)}{dt} \right]_{t=0} = \frac{a_{AB}}{\ln(10)} (10^{-M_A^{\lambda_{irr}}(0)} - 1) \quad (4c)$$

These further relationships (Eqs. (4b) and (4c)) allow us to rewrite Eq. (3c) as

$$M_A^{\lambda_{irr}}(t) = \text{Log} \left[1 + \frac{10^{M_A^{\lambda_{irr}}(0)} - 1}{10^{-M_A^{\lambda_{irr}}(0)} - 1} \ln(10) \left(\frac{m_A^{\lambda_{irr}}(0)}{a_{AB}} \right) e^{-a_{AB} t} \right] \quad (5)$$

This equation (Eq. (5)) is applicable when the same wavelength is used for both irradiation and observation, $\lambda_{irr} = \lambda_{obs}$ (i.e. $\varepsilon_A^{\lambda_{irr}} = \varepsilon_A^{\lambda_{obs}}$) and the optical path lengths for irradiation and observation are equal ($l_{irr} = l_{probe}$).

A pair of more general equations that allow the monitoring of both species via the total absorbance of the system $M_{Tot}^{\lambda_{obs}}(t) = \varepsilon_A^{\lambda_{obs}} C_A(t) l_{probe} + \varepsilon_B^{\lambda_{obs}} C_B(t) l_{probe}$ at a wavelength other than λ_{irr} , and which impose no constraints on the extinction coefficients of the species or the optical path lengths for irradiation and observation (i.e. $\lambda_{irr} \neq \lambda_{obs}$, $\varepsilon_A^{\lambda_{irr}} \neq \varepsilon_A^{\lambda_{obs}} \neq \varepsilon_B^{\lambda_{obs}} \neq 0$ and $l_{irr} \neq l_{probe}$) can be derived from a combination of the mass balance equation, Eq. (2a) and either Eq. (3c) or Eq. (5), as

$$M_A^{\lambda_{irr}}(t) = (M_{Tot}^{\lambda_{obs}}(t) - \varepsilon_B^{\lambda_{obs}} C_0 l_{probe}) \frac{\varepsilon_A^{\lambda_{irr}}}{\varepsilon_A^{\lambda_{obs}} - \varepsilon_B^{\lambda_{obs}}} \left(\frac{l_{irr}}{l_{probe}} \right) \quad (6a)$$

$$M_{Tot}^{\lambda_{obs}}(t) = \varepsilon_B^{\lambda_{obs}} C_0 l_{probe} + \frac{\varepsilon_A^{\lambda_{obs}} - \varepsilon_B^{\lambda_{obs}}}{\varepsilon_A^{\lambda_{irr}}} \left(\frac{l_{probe}}{l_{irr}} \right) \times \text{Log} \left[1 + (10^{\varepsilon_A^{\lambda_{irr}} l_{irr} C_A(0)} - 1) \times e^{-(\phi_{AB}^{\lambda_{irr}} \varepsilon_A^{\lambda_{irr}} l_{irr} I_0^{\lambda_{irr}} \ln(10)) t} \right] \quad (6b)$$

These equations may be used to analyse $M_{Tot}^{\lambda_{obs}}(t)$ data directly (Eq. (6b)) or derive values of $M_A^{\lambda_{irr}}(t)$ to use in Eq. (5).

From Eq. (6b) it is also possible to derive the general formula for the quantum yield.

$$\phi_{AB}^{\lambda_{irr}} = \frac{\ln[(1 - 10^{\varepsilon_A^{\lambda_{irr}} l_{irr} C_A(0)}) / (1 - 10^{(M_{Tot}^{\lambda_{obs}}(t) - \varepsilon_B^{\lambda_{obs}} C_0 l_{probe}) (\varepsilon_A^{\lambda_{irr}} / (\varepsilon_A^{\lambda_{obs}} - \varepsilon_B^{\lambda_{obs}})) (l_{irr} / l_{probe})) t}]}{\ln(10) \varepsilon_A^{\lambda_{irr}} l_{irr} I_0^{\lambda_{irr}} t} \quad (7)$$

Note that Eqs. (6b) and (7) reduce, respectively, to Eqs. (3c) and (4c) if $\varepsilon_A^{\lambda_{irr}} = \varepsilon_A^{\lambda_{obs}}$, $l_{irr} = l_{probe}$ and $\varepsilon_B^{\lambda_{obs}} = 0$.

3. Testing the model with numerical integration results

In order to test the model equations, we have simulated the kinetics of AB systems by using various sets of parameter values

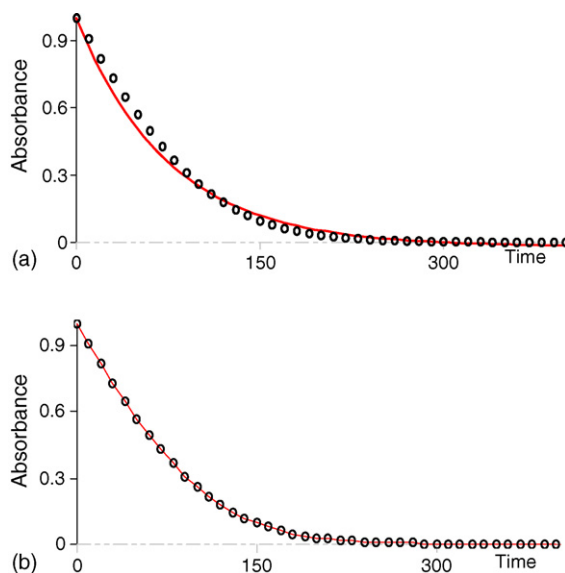


Fig. 1. Fourth-order Runge-Kutta integration of Eq. (1a) (circles); calculation based on data of Table 1 for the disappearance of the initial species. The kinetic data are incompatible with mono-exponential models (line in (a)), but are well reproduced by the theoretical model (line in (b)).

to feed a fourth-order Runge-Kutta numerical integration of Eq. (1a). Kinetic traces have been constructed for both depletion of the initial species A (recorded at $\lambda_{irr} = \lambda_{obs}$) or the appearing product B recorded at $\lambda_{obs} \neq \lambda_{irr}$ (Figs. 1 and 2, respectively, and Table 1 are given here for illustration). These calculated curves are found to be poorly fit by a pure mono-exponential model (Figs. 1a and 2a). Conversely and irrespective of the actual observation wavelength (Figs. 1b and 2b) and/or the parameter sets (not shown), the kinetic traces are rigorously reproduced by the theoretical models (Eqs. (3c) and (5)). Fig. 3 illustrates the level of agreement between the simulated data obtained from the Runge-Kutta calculation and Eq. (3c). These findings represent a validation of the theoretical model; and therefore, demonstrate that numerical integration methods are no longer required to investigate such kinetics.

4. Application example

For the classical example of the photoreduction of potassium ferrioxalate, whose kinetics is considered to occur via a single photochemical step ($\text{Fe}^{3+} \xrightarrow{h\nu} \text{Fe}^{2+}$), where the experimental data were analysed by the Runge-Kutta method [33], and the integration of the unimolecular photoreaction

differential equation by the Simpson's numerical method [34], could now be modelled by using Eq. (3c). It is also the case for systems such as the kinetics of meso-diphenylheliathrene [18] where the application of our kinetic model should be straightforward, hence replacing the approximation method employed so far. However, only a few photochemical systems comprising an inter-conversion between two species, present a specific spectral

Table 1
Basic data used to perform Runge-Kutta methods as presented in Figs. 1 and 2

C_0 (M)	$\phi_{AB}^{\lambda_{irr}}$	$\epsilon_A^{\lambda_{irr}}$ ($M^{-1} \text{ cm}^{-1}$)	I_0 ($\text{Einst s}^{-1} \text{ dm}^{-3}$)	$\epsilon_A^{\lambda_{obs}}$ ($M^{-1} \text{ cm}^{-1}$)	$\epsilon_B^{\lambda_{obs}}$ ($M^{-1} \text{ cm}^{-1}$)
2.94×10^{-5}	0.6	34,000	5.1×10^{-7}	–	27,789

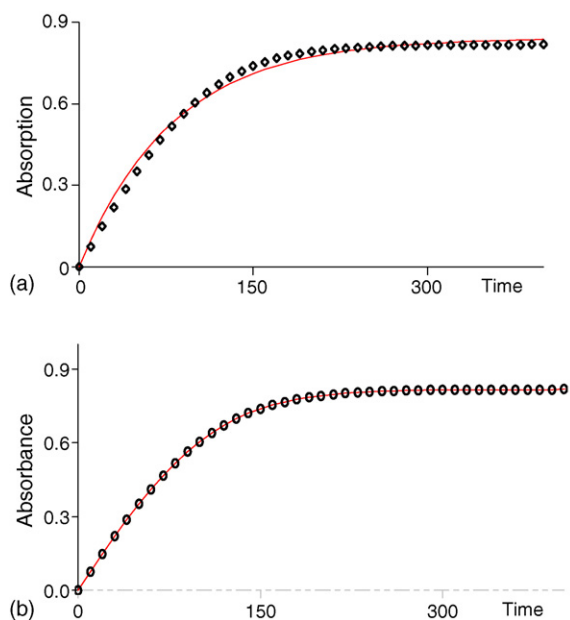


Fig. 2. Kinetic data points supplied by a fourth-order Runge-Kutta integration, using parameter values from Table 1, for the appearance of the photoproduct (species B). The kinetic data are incompatible with mono-exponential models (line in (a)), but are well reproduced by our theoretical model (line in (b)).

region where the reactant absorbs and the photoproduct does not [1–10,18,20]. Foremost amongst these are many photochromic compounds where the spectra of the initial and final species overlap throughout the ultraviolet, but may differ in the visible region (a variation that indicates the difference in chromism between the species). One can use this feature to advantage if the coloured and colourless species are thermally stable, as it is the case for many AB photochromes. These systems are excellent candidates to test our model. In this case, the species of interest (A) can be synthesised photochemically and directly monitored in solution (without being physically isolated). For the present study, we have used the diarylethene derivative **1**,

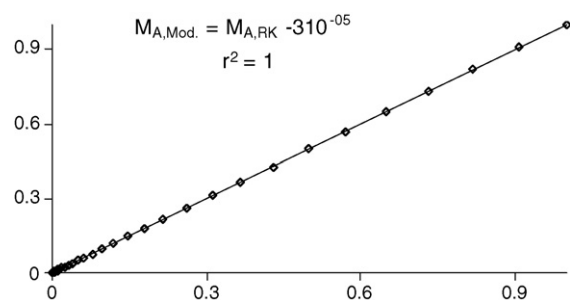
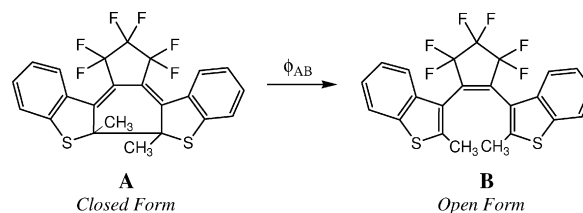


Fig. 3. Representation of calculated R-K integration absorbances ($M_{A,RK}$) against those generated by the model equation, Eq. (3c) ($M_{A,Mod.}$) as reported in Fig. 1b (r is the correlation coefficient).



Scheme 2.

both of whose isomers are thermally stable. Photoirradiation of the commercially available “open-form” species by UV light causes an electrocyclic closure of the central ring and the production of a red-coloured isomer. The closed-form species can subsequently regenerate the original system if it is submitted to visible light ($\lambda_{irr} > 400 \text{ nm}$). The opening/closure cycles can be repeated more than 10^4 times for **1** without serious degradation [22,26]. These features have made diarylethenes important basic materials for many technological applications including photo-switches, optoelectronic, optical memory and display devices [2,3,10,18–32].

In the present experimental investigation we consider the ring-opening reaction, i.e. the AB(1 ϕ) system as given in Scheme 2, performed by subjecting the coloured species (Fig. 4) to visible (437- or 517-nm) light and monitoring the temporal disappearance of its signal in solution (Fig. 5). The kinetic data have been recorded using a single irradiation/observation wavelength. The kinetic law (Eq. (6b)) rigorously fits the experimental traces yielding the results reported in Table 2. This agreement indicates that Eq. (6b) faithfully models the progressive photochemical reaction of the closed-form isomer. These results also confirm that the closed-form is the unique species in the medium that reacts to the visible light and completely regenerates the open-form (this conclusion is drawn because Eq. (6b) (like Eq. (3c)) is only applicable if both the latter conditions are met). The quantum yield values at the two irradiation wavelengths are different (Table 2), indicating that the visible irradiation wave-

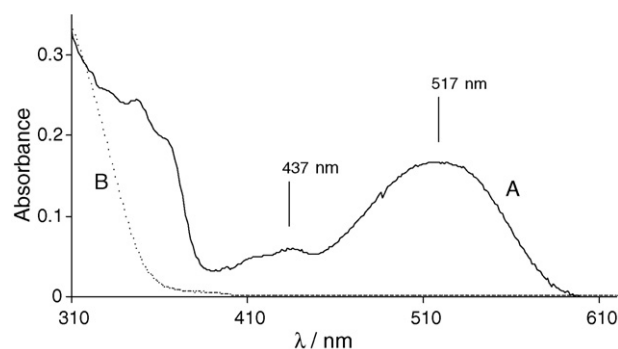


Fig. 4. Spectra of closed and open forms (A and B, solid and dotted lines, respectively) in hexane at 15°C.

Table 2

Experimental parameter values^a and the determined absolute values for the direct forward quantum yield of **1** in hexane at two different irradiation wavelengths

λ_{irr} (nm)	a_{AB} (s ⁻¹)	$\varepsilon_{\text{A}}^{\lambda_{\text{irr}}}$ (M ⁻¹ cm ⁻¹) ^b	I_0 (Einst s ⁻¹ dm ⁻³)	$\phi_{\text{AB}}^{\lambda_{\text{irr}}}$ ^c
517	1.05×10^{-2}	9.10×10^3	1.09×10^{-6}	2.42×10^{-1}
437	5.91×10^{-3}	3.56×10^3	1.31×10^{-6}	2.81×10^{-1}

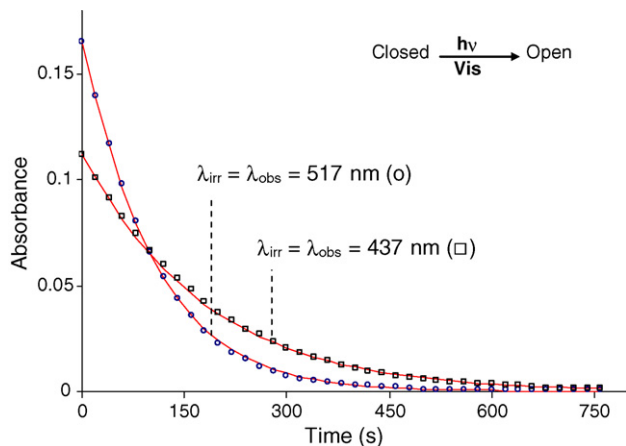
^a The initial concentration of the closed-form is $C_0 = 1.82 \times 10^{-5}$ M and l_{irr} is 2.1 cm.^b The spectrum of the closed-form isomer and $\varepsilon_{\text{A}}^{517}$ have been reported in Ref. [25]. $\varepsilon_{\text{A}}^{437}$ was calculated accordingly.^c Eq. (6b) has been employed for the determination of the quantum yields.

Fig. 5. Photokinetic traces of **1** in hexane solution (1.82×10^{-5} M (○) and 3.28×10^{-5} M (□); 15 °C) at two irradiation wavelengths in the visible. Experimental data (circles and squares) are readily fit by the theoretical model, Eq. (6b) (lines).

length affects the cycloreversion efficiency of **1**, even though the values only differ by 14%. Unsurprisingly $\phi_{\text{AB}}^{437} > \phi_{\text{AB}}^{517}$. Both these values (ϕ_{AB}^{437} and ϕ_{AB}^{517}), are however found to be smaller than the ones 0.41 [27] and 0.35 [28] reported earlier by Irie and co-workers for ϕ_{AB}^{517} of **1** in hexane, and which have been estimated using comparative methods [26,28].

5. Conclusion

The theoretical kinetic law that we have established through a closed-form integration for photochemical AB(1 ϕ) systems, allows the setting of a useful definition for the quantum yield of a unimolecular reaction. It has also been proven to be effective in describing the experimental data relating to the photoreaction of a diarylethene isomer. It has allowed the direct determination of the absolute value for the quantum yield of this isomerization. In addition, we have shown that this log–exp law can replace numerical integration methods for such systems. This model might have potential to be exploited in optimising the design of photochromes useful for information technology and/or actinometry.

6. Experimental

The diarylethene derivative (**1**) (1,2-bis[2-methylbenzo[*b*]-thiophen-3,3,4,4,5,5-hexafluoro-1-cyclopentene) was purchased from TCI Europe nv and was used without further purification. The solvent hexane was spectrophotometric

grade and supplied by Aldrich. The absorption spectra and kinetic profiles were recorded on an Agilent 8453 diode array spectrophotometer. The sample holder (designed for a 1-cm cell, i.e. $l_{\text{probe}} = 1$ cm) is equipped with a temperature control Peltier system model Agilent 8453. The irradiation equipment was manufactured by Photon Technology International Corporation. The light source was an Ushio 1000 W xenon arc-lamp located in a housing shell model A6000 and powered by a model LPS-1200 power supply. The lamp housing was connected to a model 101 monochromator, which is a special f/2.5 monochromator with a 1200 groove/300 nm blaze grating to allow irradiation wavelength selection. The excitation beam was guided through an optical fibre to impinge upon the top of the sample cuvette. Hence, the directions of the irradiation and analysis light beams were perpendicular. The incident light intensities were measured on Radiant Power/Energy meter model 70260. The measurements have less than 5% standard deviation. The sample was maintained at 15 °C and was stirred continuously during the experiment. A Levenberg–Marquardt iterative programme within the Origin 6.0 software package were used to run the non-linear fitting and the determination of the best fit curves. The theoretical numerical integration has been constructed on the basis of the fourth-order Runge-Kutta method (results obtained from a homemade programme).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2006.10.030.

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