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Kinetics of photobleaching of Aberchrome 540 in various solvents: solvent effects

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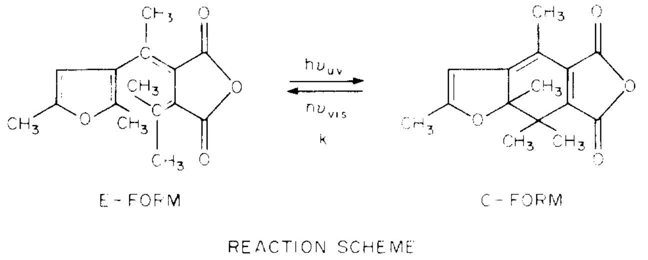
Abstract

The fulgide known as Aberchrome 540, E-form ((E)-α-(2,5-dimethyl-3-furylethylidene)(isopropylidene) succinic anhydride), is a photochromic dye which undergoes conrotatory ring closure when irradiated with UV light at $\lambda > 300$ nm to give a red dye, C-form (7,7a-dihydro-2,4,7,7,7a-pentamethylbenzo[b]furan-5,6-dicarboxylic anhydride). The C-form is bleached with white light to revert back to the E-form. The photobleaching reaction was conducted in a number of solvents of various polarities over the temperature range 303–333 K. The extent of bleaching was monitored spectrophotometrically by measuring the absorbance of the C-form at $\lambda_{max} = 493$ nm. The reaction is pseudo-first-order allowing for the extraction of the apparent rate constants and the apparent activation energies. The solvent polarity affects the rate of the photoinduced reaction and, in addition, other factors, such as the solvent viscosity and hydrogen bonding, are important.

Keywords: Photobleaching; Aberchrome 540; Kinetics; Solvent; Solvent effects; Photoisomerization

1. Introduction

Photochromic reactions of dyes have been the subject of a number of investigations in recent years. This is due to their potential applications in areas such as imaging and eraseable optical memory [1–3], electro-optical devices and components [4]. Many investigations, representing the commonly studied dyes, have been treated in a monograph [5]. The work on a number of dyes trapped in various polymer matrices has also been reviewed [6]. While polymers are the media of choice for most eventual applications, they often cause difficulties in the analysis of the results due to the interactions between the polymers and the dye. For example, a first-order photochromic reaction in solution deviates from first-order when reacted in a polymer medium, and has led to the proposal of various kinetic models, i.e. kinetic matrix effect [7], composite exponential decay [8] and dispersive processes [9–11]. There are two major contributing factors to the departure from a first-order plot: inadequate free volume in the microenvironment of the dye sites, thereby restricting the motions of the dye molecules during the photoinduced change, and/or the existence of more than a single conformer of the dye molecules. Details of this discussion have been published elsewhere [12].



Scheme 1.

We have been working with one of the photochromic fulgides known as Aberchrome 540 trapped in a number of polymer matrices [12–14]. In its ring-opened E-form, the dye is amber. When it is irradiated with UV light, it undergoes conrotatory ring closure to give a red, C-form. On irradiation with visible light, the C-form is reverted to the E-form with the rate constant k as shown in Scheme 1. The latter reaction is known as the photobleaching reaction of the dye. Both the $C \rightarrow E$ and $E \rightarrow C$ reactions in polymer films have been investigated in our laboratory [12–14].

The results of our investigations show that the polarity of the medium may affect the rates of the reactions. In an attempt to obtain more information without interference due to the limited mobility of solid polymer media, the photobleaching of the red dye ($C \rightarrow E$) has been examined in a number of solvents of varying polarity. The results of the investigation form the basis of this paper.

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2. Experimental procedures

Aberchrome 540 in its amber form was supplied by Aberchromic Ltd., Cardiff. The solvents used were *n*-heptane, toluene, 1-pentanol, ethanol, ethyl acetate and acetonitrile. They were purchased from Aldrich; each was dried and distilled collecting only the middle fractions.

The dye solutions in selected solvents were prepared at a concentration of 6×10^{-5} M. Each solution was placed in a quartz reactor and was irradiated with UV light emitted from a lamp (Black Rays) fitted with a glass filter transmitting $\lambda > 300$ nm. This procedure converted the amber E-form to the red C-form until the maximum conversion had been attained as indicated by the maximum absorption of the red dye at $\lambda_{max} = 493$ nm. The sample was then placed in a heating stage whose temperature was regulated and maintained to ± 0.2 K. The continuously stirred solution was then bleached with white light emitted from a tungsten lamp (General Electric) for various periods of time, and the extent of bleaching of the red dye was monitored by measuring the decreasing absorbance at λ_{max} with a spectrophotometer (Spectronic 2000, Bausch & Lomb). The experiments were conducted in the temperature range 303–333 K. Higher temperatures were avoided due to possible thermal degradation of the dye. The incident intensity of visible light was measured with a chemical actinometer (using Aberchrome 540 [15]) to be 4×10^{-9} einstein cm^{-2} s^{-1} at a power output of 75 W. This chemical actinometer was found to be satisfactory in previous applications [16].

3. Results and discussion

Plots of $\ln[A(t) - A(\infty)]$ against time (s) were made for each temperature and typical results are shown in Fig. 1 for a non-dipolar solvent (*n*-heptane) and in Fig. 2 for a dipolar solvent (acetonitrile). This allows for the extraction of the apparent rate constants k. The values of $\ln k$ at various temperatures were plotted against $1/T$ (K^{-1}) to obtain the overall activation energies (E_a) of the reaction in each solvent as shown in a sample plot (Fig. 3) for the photobleaching of the red dye in acetonitrile. The apparent rate constants k for the reaction in various solvents at 303 K and the overall E_a values are collected in Table 1. For comparison, some physical properties of the solvents, such as the relative permittivity (ϵ_r), dipole moment (μ), viscosity (η) and $E_T(30)$, are collected in Table 2. The $E_T(30)$ values are the empirical parameters of solvent polarity obtained from the use of Reichardt's dye [20].

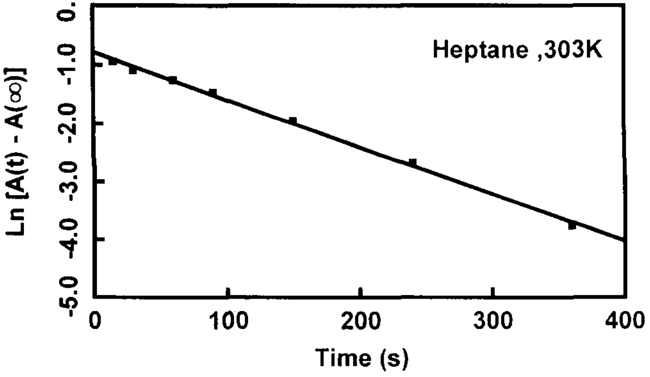

Fig. 1. Plot of $\ln[A(t) - A(\infty)]$ against time (s) for the reaction in a non-dipolar liquid (*n*-heptane) at 303 K.

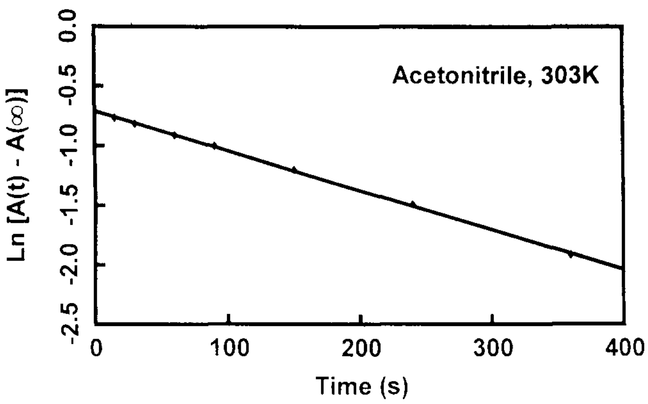

Fig. 2. Plot of $\ln[A(t) - A(\infty)]$ against time (s) for the reaction in a dipolar liquid (acetonitrile) at 303 K.

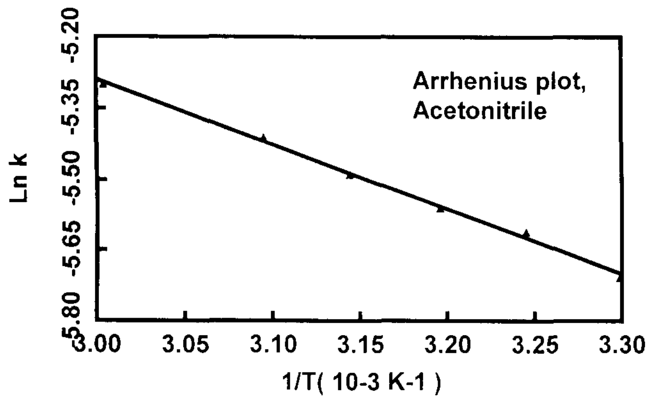

Fig. 3. Arrhenius plot of $\ln k$ (k in s^{-1}) vs. $1/T$ (K^{-1}) for the reaction in acetonitrile.

Table 1

Comparison of the apparent rate constants (k) at 303 K and the apparent activation energies (E_a) for the photobleaching of Aberchrome 540 in various solvents

Solvent	k[a] (10^{-3} s^{-1})	E_a[b] (kJ mol^{-1})
n-Heptane	8.11	9.95
Toluene	6.71	8.88
1-Pentanol	6.56[c]	4.57[c]
Ethanol	6.72	4.23
Ethyl acetate	5.78	7.78
Acetonitrile	3.32	11.39

[a] Error in k is approximately $\pm 6\%$.
[b] Error in E_a is approximately $\pm 12\%$.
[c] From Ref. [17].

Table 2
Collection of various properties, i.e. relative permittivity (ϵ_r), dipole moment (μ), solvent polarity parameter ($E_T(30)$) and viscosity (η) of selected solvents [a]

Solvent	ϵ_r [b]	μ [c] (10^{-30} C m)	$E_T(30)$ [d] (kJ mol^{-1})	η [e] (mPa s)
n-Heptane	1.92(293)	0.0	130.1	0.386
Toluene	2.38	1.0	141.8	0.568 [f]
1-Pentanol	13.90	5.7	205.4	3.619
Ethanol	24.55	5.8	217.1	1.108 [g]
Ethyl acetate	6.02	6.1	159.4	0.441
Acetonitrile	35.94	11.8	190.8	0.345

[a] All values are at 298 K, unless specified otherwise.
[b] Relative permittivities taken from Ref. [18].
[c] From Ref. [19].
[d] Converted from $E_T(30)$ in kcal mol^{-1} of Reichardt [20]. Conversion factor: 1 kcal mol^{-1} = 4.148 kJ mol^{-1}.
[e] Unless stated otherwise, values are taken from Ref. [21].
[f,g] Interpolated from the data given in Ref. [21].

3.1. Factors affecting the rate of a chemical reaction

In order to allow for a proper discussion of the current work, an overview of the common factors that can influence the rate of a non-ionic chemical reaction is given. These factors are: (a) the polarity of the medium; (b) the viscosity of the solvent; (c) the reaction temperature; (d) hydrogen bonding. Theoretical aspects dealing with factors (a) and (b) are briefly discussed below.

The effect of solvent polarity on the rate of a photoisomerization reaction has been treated in recent work [22–25]. The influence of the medium polarity is linked to the activation energy of the reaction by [25]

$$E_a = E_a^0 \pm A[E_T(30) - 130.1] \tag{1}$$

where the sign in front of A is plus or minus depending on whether the polarity ($E_T(30)$) causes an increase or decrease in E_a, respectively. $E_T(30)$ is the solvent polarity parameter in kJ mol^{-1}, shown in contrast with the corresponding value of non-dipolar *n*-heptane (130.1), E_a^0 is the polarity-independent barrier height and parameter A depends on the change in barrier height with the solvent polarity. For a medium whose polarity causes an increase in E_a, the rate constant k' (applicable to a set of experiments whose solutions are isoviscous) is

$$k' = C \exp\{-A[E_T(30) - 130.1]/RT\} \exp(-E_a^0/RT) \tag{2}$$

where C is the Arrhenius pre-exponential factor.

The rate of a reaction which involves the twisting or rotating of a reactant in order to form the product must overcome the viscous drag (e.g. in the photoisomerization of stilbene and its derivatives), and its rate constant may be represented by [22]

$$k_i = F(\zeta) \exp(-E/RT) \tag{3}$$

where E is the viscosity-independent activation energy and $F(\zeta)$ is the reduced rate (isomerization) which may be expressed as

$$F(\zeta) = \zeta\omega_r/(4\pi\omega_b I_r)\{[1 + (\omega_b I_r/\zeta)^2]^{1/2} - 1\} \tag{4}$$

where ζ is the friction coefficient, ω_r is the reactant well frequency, ω_b is the barrier frequency and I_r is the reduced moment of inertia. If it is assumed that $\zeta \propto \eta$, Eq. (4) may be converted to a hydrodynamic form

$$F(\zeta) = \frac{A_1\eta}{A_2}\left\{\left[1 + \left(\frac{A_2}{\eta}\right)^2\right]^{1/2} - 1\right\} \tag{5}$$

where A_1 and A_2 are adjustable parameters that relate to the structural parameters of the solute particle and the frictional solute–solvent coupling. It should be emphasized that Eqs. (1)–(5) are empirical. Another factor which needs to be considered is the temperature-dependent viscosity (η) which may be expressed as [26–28]

$$\eta = \eta_0 \exp(E_v/RT) \tag{6}$$

where η_0 is the temperature-independent constant relating to the viscosity of the liquid and E_v is the activation energy for viscous flow. Eqs. (3), (5) and (6) may be combined to give

$$k_i = (B/\eta_0) \exp[-(E+E_v)/RT] \tag{7}$$

where E is the activation energy (independent of viscosity) and B is a parameter which gives the characteristic reaction timescale. With this information, it is now possible to relate and discuss some of our results.

The first-order plot for each set of data, as shown in Figs. 1 and 2, gives a straight line with a correlation coefficient better than 0.98 for the reaction in all the solvents investigated. The Arrhenius plot provides a single value of the apparent (overall) activation energy for each solvent as shown in Fig. 3.

3.2. Specific solvent effects on the apparent rate constants k

3.2.1. Effect of medium polarity on k

Inspection of Table 1 for the k values of the photoinduced bleaching of the dye shows that k (s^{-1}) is largest for non-dipolar *n*-heptane (8.11×10^{-3}) and smallest for dipolar acetonitrile (3.32×10^{-3}). For the weakly dipolar toluene (6.71×10^{-3}) and the moderately dipolar solvents (1-pentanol (6.56×10^{-3}), ethanol (6.72×10^{-3}) and ethyl acetate (5.78×10^{-3})), the k values are comparable and fall between those of *n*-heptane and acetonitrile. Thus the general trend appears to be that the k value decreases with increasing solvent dipole moment. Such a trend is also observed when the polarity parameter $E_T(30)$ is used instead of the dipole moment. This agrees qualitatively with Eq. (2). However, the polarity effect of the solvent cannot be the only factor influencing the magnitude of the k values. For example, the dipole moment μ (in 10^{-30} C m) of toluene (1.0) is less than μ for 1-pentanol (5.7) and ethanol (5.8) as shown in Table 2, yet the reaction in these solvents yields comparable k values (within the limits of experimental error) as shown in Table 1, and other medium effects need to be considered.

3.2.2. *Viscosity effect on k*

For photobleaching, the ring-closed reactant (C) is converted to the ring-opened product (E). The molecule must undergo rotation in order to bring about the change. It is expected that the viscous drag of the solvent will influence the reaction rate. For non-associated liquids with zero or small dipole moments, such as heptane and toluene, the k value decreases from 8.11×10^{-3} s^{-1} to 6.71×10^{-3} s^{-1} respectively, while the viscosity increases from 0.386 to 0.568 mPa s (1 P = 100 mPa s). Such a change in k with the corresponding change in η is in qualitative agreement with Eq. (7), i.e. k decreases with an increase in η_0 and E_v. For associated liquids, such as 1-pentanol and ethanol, the above relation between the viscosity and k does not hold possibly due to the effect of hydrogen bonding (see below).

3.2.3. *Effect of hydrogen bonding on k*

For the reaction in solvents such as 1-pentanol and ethanol, whose viscosities and dipole moments are 3.619 and 1.108 mPa s and 5.7×10^{-30} and 5.8×10^{-30} C m respectively, the effect of the dipolar medium should be comparable. Thus if the reaction rate is only affected by the viscosity, it should be expected that k in 1-pentanol should be less than k in ethanol due to the higher viscosity of the former than the latter. However, the rate constants k for the reaction in 1-pentanol and ethanol are 6.56 and 6.72 s^{-1} respectively which are approximately the same (within experimental error). The exact reasons for the comparable rate constants, despite the differences between their viscosities, are unknown. It is plausible that this may be explained on the basis of the formation of intermolecular hydrogen bonds between the solvent and dye molecules and/or the presence of different types of molecular associates for different alcohols. These effects may cause the reaction rate to be faster in 1-pentanol than in ethanol, consequently compensating for the viscosity which should have the opposite effect. It is not unreasonable to expect that the molecular associates formed from the two types of alcohols should be different due to the difference in their monomeric structures. Furthermore, reactions in alcohols are known to generate anomalous effects, e.g. alcohols can cause negative or positive synergistic effects [17,29] and enantioselectivity of enzyme reactions [30–32] depending on the nature of the reactants and the alcohol used, either as solvent or co-solvent. The anomalous physicochemical behaviour of various pentanols has been the subject of research in recent years [17,26,33,34].

Evidence to support intermolecular hydrogen bonding between the dye and alcohol molecules may be advanced from our IR results of the dye dissolved in various solvents, the details of which have been published elsewhere [17]; only relevant features are described here. The coupling frequencies belonging to the carbonyl groups of the succinic anhydride moiety of the red dye in non-dipolar and non-associated *n*-heptane appear at 1817 and 1769 cm^{-1}. The corresponding frequencies are shifted to 1814 and 1764 cm^{-1} in associated liquids such as 1-pentanol. Such a shift to lower wavenumber (relative to *n*-heptane) in dipolar protic solvents is characteristic of the carbonyl stretching mode [35,36]. Our results show that the frequency shifts are caused by the polarity as well as the ability of the solvent to form hydrogen bonds with the red dye. The formation of hydrogen bonds between the O atoms of the carbonyl groups and the H atoms of the –OH groups (of alcohols) may affect the stability of the dye molecules, thereby changing the reaction rate. This point may be partially substantiated in the ensuing discussion related to the overall activation energies.

It should be pointed out that each of the E_a values shown in Table 1 represents the overall or apparent (thermal) activation energy due to composite effects, i.e. the intrinsic activation energy E_0, which is normally small (if any) for a photoinduced reaction, the activation energy due to viscous flow E_v, the barrier due to dipolar interaction with the medium and, for associated liquids, the barrier to break the hydrogen bond(s). Thus the term apparent activation energy is adopted. Likewise, the rate constant k is not an absolute constant; rather it is the rate constant due to these composite effects. Consequently, it is called the apparent rate constant. From Table 1, the value of E_a for toluene is almost twice the magnitude of E_a for ethanol or 1-pentanol (with comparable E_a values in the alcohols). However, the k values are approximately the same. These results suggest that the pre-exponential factor (A') for the reaction in alcohols is smaller than that in toluene. For a unimolecular reaction in solution, as examined here, A' may be derived from transition state theory [37]: $A' = e(k_BT/h)\exp(\Delta S^{\#}/R)$, where k_B is the Boltzmann constant and $\Delta S^{\#}$ is the entropy of activation. This implies that the value of $\Delta S^{\#}$ for the reaction in alcohols is less than that in toluene. For these values of k and E_a, the $\Delta S^{\#}$ values are negative; those in alcohols are more negative than that in toluene, to the extent of approximately 15 J mol^{-1} K^{-1}. This may be interpreted as a better ordered transition state complex in alcohol than in toluene. Such a situation could arise from the possible presence of intermolecular hydrogen bonds between the dye and alcohol molecules. This would be consistent with our previous IR results, which show the ability of the red dye in its ground state to form hydrogen bonds with 1-pentanol [17], provided that the geometry of the dye molecule in its transition state complex is not altered much from its ground state.

There is one aspect of the investigation which merits further discussion, i.e. the possibility of dye–dye interactions. This point was tested by increasing the dye concentration by a factor of 1.5, and no significant difference was observed in the value of k within experimental error. Therefore, at the concentration of the dye used in these experiments, complications due to interactions between the dye molecules may be neglected.

4. Conclusions

It has been shown in this investigation that the polarity of the solvent can retard the rate of photobleaching of the dye. However, the polarity is not the only factor affecting the rate of the photochromic reaction. Other factors, such as the viscosity and the ability of the solvent molecules to form intermolecular hydrogen bonds with the dye, may also affect the rate of the reaction.

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