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Photokinetic study of a novel phenylfulgide: effects of solvents on its photochromic reaction

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Abstract

A photokinetic method was used to study the photochromic reaction of a novel fulgide, (*E*)-2-isopropylidene-3-[1-(3,4-dimethoxyphenyl)ethylidene]-3-isopropylidene succinic anhydride. It was found that the photochromic reaction depends on the solvent polarity. The apparent ring-closure rate decreased with increasing solvent polarity, while the rate of *E* to *Z* isomerization increased. It was supposed that there were two kinds of conformation in the excited states. Increasing the solvent polarity favoured the twisted conformation, which accelerated the *E* to *Z* photo isomerization, inhibiting the electrocyclic reaction. © 1997 Published by Elsevier Science S.A.

Keywords: Fulgide; Photochromic reaction; Photokinetics; Solvent effects

1. Introduction

Fulgides are important organic photochromic compounds which have found use in optical recording materials and chemical actinometry [1–4]. When irradiated by UV light, the *E*-form of an aromatic substituted fulgide processes an intromolecular [4,2] photocycloaddition to give its coloured form of 1,8a-dihydronaphthalene (1,8a-DHN). In the meantime, the *E–Z* isomerization about one double bond also occurs [2,5]. In a previous paper [6], we reported a photokinetic study on (*E*)-2-[1-(2,5-dimethyl-3-furyl)-ethylidene]-3-isopropylidene succinic anhydride, named commercially Aberchrome 540™. We found that this famous chemical actinometer could not be used repeatedly as the *E–Z* isomerization about one double bond reduced the apparent quantum yield of the photocycloaddition reaction. Recently, we synthesized a novel phenylfulgide processing two methoxy groups in the phenyl moiety and tried to study its photokinetic behaviour.

The (*E*)-2-isopropylidene-3-[1-(3,4-dimethoxyphenyl)-ethylidene]-3-isopropylidene succinic anhydride (VF, Scheme 1) was synthesized by Stobbe condensation. As we only know the spectroscopy of this (*E*)-form, we performed the photokinetic experiment as described by Ilge [7] for a four-component system. Two beams of light, 365 nm and 494 nm, were used to irradiate the toluene solution of VF simultaneously, the whole reaction was followed spectroscopically by a diode array spectrophotometer during irradiation. To our surprise, the initial spectrum remains the same for a period of 5 min. It is necessary to find another method to solve this problem.

Fig. 1 shows the reaction spectrum of VF in toluene. The absorbance data at the wavelengths 300, 336, 350, and 366 nm are plotted vs. the absorbance at 528 nm at all reaction times in Fig. 2 (absorbance (*E*) diagram). From the good linear relationships it can be assumed that the photoreaction shows uniform reaction. This means that a single reaction step is found, the overall reaction can be considered to follow the mechanism proposed by Mauser [8].

2. Fundamental kinetics

The rate law for the reaction

$$C \underset{\phi_2}{\overset{\phi_3}{\leftrightharpoons}} A \xrightarrow{\phi_1} B$$

is given by

$$\frac{\mathrm{d}a}{\mathrm{d}t} = -(\phi_1 + \phi_2)1000 I_0 \epsilon_A{}' F(E')a(t) + \phi_3 1000 I_0 \epsilon_C{}' F(E')c(t) \qquad (1)$$

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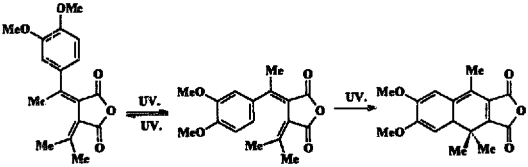

C (Z-VF) A (E-VF) B (DHN)

Scheme 1.

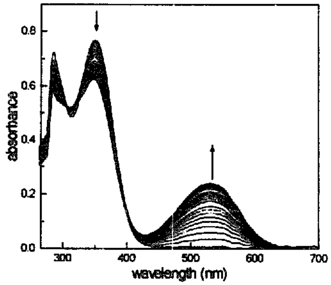

Fig. 1. Reaction spectrum for the photoreaction of VF in toluene.

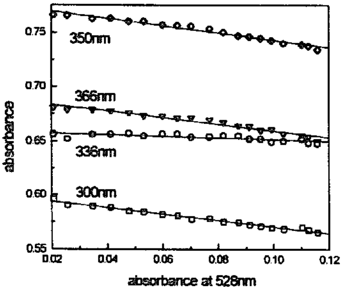

Fig. 2. Absorbance plots for VF in toluene. Straight lines are observed for combinations of absorbances at two wavelengths.

$$\frac{db}{dt} = \phi_1 1000 I_0 \epsilon_A' F(E') a(t) \tag{2}$$

$$\frac{dc}{dt} = -\phi_3 1000 I_0 \epsilon_C' F(E') c(t) + \phi_2 1000 \epsilon_A' I_0 F(E') a(t) \tag{3}$$

Also

$$E^{\lambda}(t) = E^{\lambda}_{A}(t) + E^{\lambda}_{B}(t) + E^{\lambda}_{C}(t) \tag{4}$$

$$a_0 = a(t) + b(t) + c(t) \tag{5}$$

Where I_0 is the intensity of monochromatic radiation (mol-photons cm^{-1} s^{-1}), ϕ_1, ϕ_2, and ϕ_3 are the differential photochemical quantum yields of photo reactions A → B, A → C, and C → A respectively. ϵ'_A, ϵ'_C are the molar decadic absorption coefficients of compounds A and C at the irradiation wavelength, $F(E') = (1 - 10^{-E'})/E'$) is the photokinetic factor with absorbance $E'(t)$ at the irradiation wavelength at time t. $E^{\lambda}_{A}(t)$, $E^{\lambda}_{B}(t)$ and $E^{\lambda}_{C}(t)$ are the absorbances of compounds A, B, and C at the measured wavelength at time t respectively. $E^{\lambda}(t)$ is the total absorbance of the mixture at the measured wavelength at time t. $a(t)$, $b(t)$, and $c(t)$ are the concentrations of compounds A, B, and C at time t separately. a_0 is the concentration of compound A at the beginning of the reaction.

At the beginning period of UV irradiation, the concentration of C is approximately zero compared with that of A. The initial rate laws Eq. (1) and Eq. (3) can be rewritten as follows:

$$\frac{da}{dt} = -(\phi_1 + \phi_2) 1000 I_0 \epsilon_A' F(E') a(t) \tag{6}$$

$$\frac{dc}{dt} = \phi_2 1000 \epsilon_A' I_0 F(E') a(t) \tag{7}$$

Also

$$E^{\lambda}(t) = E^{\lambda}_{A}(t) + E^{\lambda}_{C}(t) \approx E^{\lambda}_{A}(t) \tag{8}$$

Then we have

$$\frac{dE^{\lambda}(t)}{dt} \approx \frac{dE^{\lambda}_{A}(t)}{dt} = -(\phi_1 + \phi_2) 1000 I_0 \epsilon_A' F(E') E^{\lambda}(t) \tag{9}$$

Integrating this equation yields

$$\ln E^{\lambda}(t) = -(\phi_1 + \phi_2) 1000 I_0 \epsilon_A' \int_0^t F(E')\, dt + \ln E^{\lambda}(0) \tag{10}$$

If $\ln E^{\lambda}(t)$ is plotted vs. $\int_0^t F(E')dt$, we obtain

$$k = -(\phi_1 + \phi_2) 1000 I_0 \epsilon_A' \tag{11}$$

The total apparent reaction speed can be derived as follows:

$$k_{obs} = \phi_1 + \phi_2 = -\frac{k}{1000 I_0 \epsilon_A'} \tag{12}$$

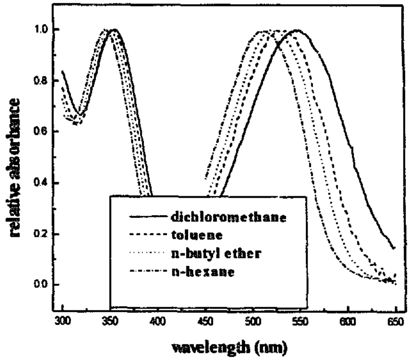

Fig. 3. The normalized absorption spectra of VF and its coloured form in various solvents.

Under the same experimental conditions, the relative apparent rate is

$$k_R = \frac{k_n \epsilon_{A0}'}{k_0 \epsilon_{An}'} \quad (13)$$

When the initial concentration remains the same, Eq. (13) can be rewritten as

$$k_R = \frac{k_n E_{A0}'}{k_0 E_{An}'} \quad (14)$$

Where k_R is the relative apparent reaction rate of the photoreaction, k_0 is the measured reaction rate of basic photoreaction, ϵ'_{A0}, E'_{A0} are the molar decadic absorption coefficient and absorption of compound A at the irradiation wavelength respectively. k_n, ϵ'_{An}, E'_{An} is the measured reaction rate, the molar decadic absorption coefficient and absorption of compound A at the irradiation wavelength of the corresponding photoreaction respectively.

3. Experimental details

The (E)-2-isopropylidene-3-[1-(3,4-dimethoxyphenyl)-ethylidene]-3-isopropylidene succinic anhydride (VF) was prepared under conditions prescribed by the procedure described before [9]. The solvents used were purified according to standard methods. A modified reaction cell was fitted in a diode array spectrophotometer (HP8452a, Hewlett-Packard) to follow the photoreaction during irradiation as described before [6]. 366 nm light from a 250 W high pressure Hg lamp was used as the excitation source in the photoreaction process. The light intensity was measured with a toluene solution of Aberchrome 540™.

4. Results and discussion

4.1. Absorption spectra

Fig. 3 shows the absorption spectra of VF and its coloured form in various solvents. Table 1 gives the corresponding maximum absorption. There are no significant changes in the absorption spectra of VF when the solvent polarity is increased; however, apparent bathochromic effects are observed for the coloured form. This implies that the presence of electron donor (methoxy group) and electron acceptor (anhydride group) moieties on phenyl fulgide derivatives leads to an intramolecular charge transfer upon exication, resulting in a solvatochromic effect. The better planarity of the coloured form of VF makes the intramolecular charge transfer process easier. As the increase in solvent polarity favoured the formation and stability of the charge transfer state [10], the absorption spectra of the coloured form processes a larger bathochromic shift than that of VF.

4.2. Photokinetic study

VF in various solvents was irradiated at room temperature. Typical $\ln E^{A}(t) \sim \int_0^t F(E')\mathrm{d}t$ relationships are shown in Fig. 4. The apparent photoreaction rate in various solvents is given in Table 2.

To investigate the influence of solvent polarity on electrocyclic reactions, we also measured the formation rate of DHN in various solvents (Fig. 5). It is obvious that with an increase in solvent polarity alone, the electrocyclic reaction rate is decreased. Particularly in the ethanol solvent, no formation of DHN can be observed.

Table 1
Maximum absorption of VF and its coloured form (DHN) in various solvents

Solvent	$E_T(30)$ (kcal mol^{-1})	λ_{max}(nm)lg(ϵ_{max}) (VF)	λ_{max}(nm) (DHN)
Hexane	31.0	344(3.82)	508
n-Butyl ether	33.0	346(3.88)	516
Toluene	33.9	352(3.89)	528
Iso-propyl ether	34.0	346(3.94)	516
1,4-Dioxane	36.0	346(3.94)	524
Tetrahydrofuran	37.4	346(3.92)	530
Chloroform	39.1	350(3.97)	528
Dichloromethane	40.7	352(3.95)	542
Acetonitrile	45.6	352(4.00)	546
Ethanol	51.9	352(3.87)	—

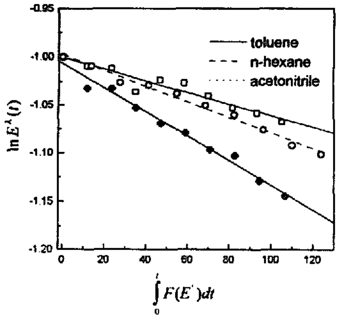

Fig. 4. $\ln E^A(t) \sim \int_0^t F(E')dt$ relationship of VF in various solvents.

Table 2
The apparent photoreaction rates of VF in various solvents [a]

Solvent	log ϵ_{366}	k ($\times 10^4$)	k_{dhn} ($\times 10^3$)	k_R
n-Hexane	3.74	1.4	0.18	1.0
Toluene	3.86	4.1	0.39	2.2
1,4-Dioxane	3.85	3.5	0.34	1.9
Dichloromethane	3.91	3.4	0.29	1.6
Chloroform	3.93	2.6	0.21	1.2
Acetonitrile	3.94	3.0	0.57	3.2
Ethanol	3.81	13.4	1.44	8.0

[a] $I_0 = 1.4323 \times 10^{-7}$ einstein s^{-1}.

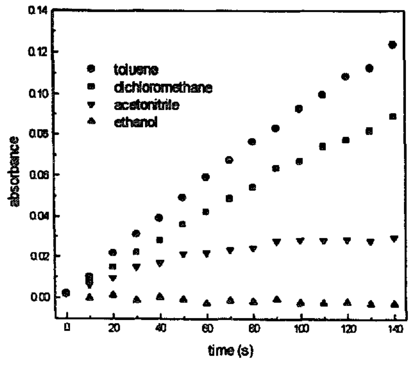

Fig. 5. The relationship between the absorbance of DHN and irradiating time.

According to Paetzold's report [2,11], phenyl fulgides had typical $\pi \rightarrow \pi^*$ photoreactivity and in the singlet state *E–Z* isomerizations about one double bond compete with electrocyclic ring closure to the coloured form under direct UV irradiation. At the beginning of photo irradiation, the photoisomerization of *Z* to *E* can be omitted, so the total reaction rate is the sum of the photoisomerization rate of VF to its *Z*-isomer and the electrocyclic reaction rate of VF to DHN. When the solvent polarity increases, the electrocyclic reaction rate decreases while the total reaction rate has no significant change. This implies that the increase in solvent polarity suppresses the electrocyclic cycloaddition reaction, and favours the *E–Z* isomerization reaction. As in direct photo irradiation, there is a 'P' state alone with twisting of the double bond in the *E–Z* isomerization. The 'P' state converts to the singlet state of the basic state via internal conversion so as to give the *E*- or *Z*-form of the compound. The (4 + 2) cycloaddition, however, can only take place via a planar transform state [12]. It has been reported that the increase in solvent polarity had little effect on either pure electrocyclic reaction or pure *E–Z* isomerization [13]. Actually, VF consists of two methoxy groups and a maleic anhydride moiety; the former is a donor and the latter an acceptor, which makes the polarity of the excited singlet state of VF greater than that of the ground state, leading to an intramolecular charge transfer process upon excitation. In less polar solvents, the excited state stabilizes to both a planar conformation and a twisted conformation, the *E–Z* isomerization and electrocyclic reaction take place simultaneously. As the solvent polarity increases, however, the twisted conformation is stabilized, which favours *E–Z* isomerization, inhibiting the electrocyclic reaction (Fig. 6).

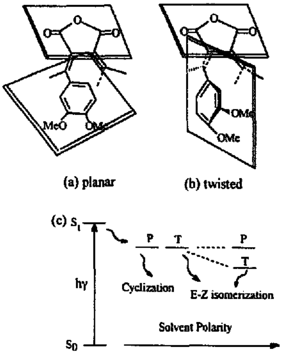

Fig. 6. Schematic illustration of the effects of solvent on the excited state of VF. (a) The planar form and (b) the twisted form of VF. (c) Excited states in solvents of various polarity. P and T denote the planar and twisted forms respectively.

5. Conclusion

A photokinetic method was used to study the photochromic reaction of VF, which showed that the photochromic reaction depended on solvent polarity. The apparent ring-closure rate decreased with increasing solvent polarity, while the rate of *E* to *Z* isomerization increased. It was supposed that there were two kinds of conformation in the excited states; increasing the solvent polarity favoured the twisted conformation, which accelerated the *E* to *Z* photo isomerization, inhibiting the electrocyclic reaction.

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