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PHOTOCHEMICAL $E \rightarrow Z$ ISOMERIZATION OF THE 1,4-DIAZABUTADIENE DERIVATIVE DIACETYLDIANIL

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Summary

UV irradiation of the 1,4-diazabutadiene derivative diacetyldianil (DADA) results in conversion into the Z,E isomer which is thermally stable at temperatures below −50 °C. The thermal back reaction that occurs after the irradiation of DADA was investigated in the temperature ranges −50 to −10 °C and 20 - 65 °C by a low temperature technique and flash photolysis respectively. The activation parameters compare well with those obtained for benzylidene aniline and its derivatives. The solvent dependence and acid catalysis suggest that the isomerization reaction has a planar inversion mechanism.

1. Introduction

1,4-diazabutadienes of the general formula

$$R^1-N \overset{R^2}{\underset{}{\diagdown}} C=C \overset{N-R^4}{\underset{R^3}{\diagup}}$$
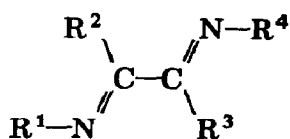
exist as E,E isomers with *s-trans* conformation in solution. Nuclear magnetic resonance and dipole moment data [1, 2] have shown that the stable conformation at room temperature is not planar. No data regarding the photochemical behaviour of 1,4-diazabutadienes (R^1, R^2, R^3, $R^4 \equiv$ H, alkyl or aryl) are available. Owing to the high isomerization barrier, the only information data published are for the diimines (R^1, $R^4 \equiv$ F; R^2, $R^3 \equiv CH_3$) and their $1E,3Z$, $1Z,3Z$ and $1E,3E$ isomers [3]. In contrast, the photochemical properties of the 2,3-diazabutadienes (azines) which are isomeric with the 1,4-diazabutadienes and of the azomethines ($R^1R^2C=NR^3$) are well characterized. The photochemically generated E,Z and Z,Z isomers of azines containing higher condensed aromatic substituents have been isolated and characterized [4]. Reversible photoisomerization is detectable at low temperatures for

aromatic azomethines such as benzylidene aniline [5, 6] and can also be induced by flash photolysis at room temperature [7]. A comparison of the photochemical behaviour of 1,4-diazabutadienes with that of the azines and the azomethines is likely to be interesting. Differently substituted 1,4-diazabutadienes (R^1, $R^4 \equiv$ phenyl, naphthyl; R^2, $R^3 \equiv CH_3$, phenyl) were synthesized for this purpose; unfortunately compounds with R^1, $R^4 \equiv$ anthranyl proved impossible to synthesize.

When the compounds were irradiated at room temperature into the longest wavelength absorption band no photochemical isomerization was detectable, whereas reversible spectral changes were observed at lower temperatures and after flash photolysis at room temperature. In the remainder of this paper the behaviour of diacetyldianil (DADA) is described in more detail.

2. Experimental details

The spectra were recorded using a UV–visible spectrophotometer (Specord UV/VIS, VEB Carl Zeiss Jena) equipped with a cell housing and cryostat constructed in the laboratory. The temperature was held constant to within ±0.5 °C. Crossed irradiation and analysing beams allowed the cell to remain fixed at exactly the same position throughout the entire irradiation and measurement period.

A conventional flash photolysis apparatus was used. The electrical energy was 1000 J and the full width at half-maximum was 13 μs. The exciting light was selected by a Schott UG 11 filter. A waveform analysing system (EMG 5500, Elektronikus Merökészülékek Gyara, Budapest) linked to a desk calculator (EMG 666, Elektronikus Merökészülékek Gyara, Budapest) was used.

The solvents were spectrograde quality (Uvasol, Merck, Darmstadt). DADA was prepared using the method of Ferguson and Goodwin [8].

3. Photoisomerization of diacetyldianil

Figure 1 shows the absorption spectra of DADA solutions in ethanol as a function of the irradiation time. Upon irradiation into the longest wavelength absorption band two isosbestic points were obtained at 310 and 267 nm. The corresponding extinction difference (ED) diagrams obtained by Mauser [9] are strictly linear, indicating a unitary reaction according to his notation. After prolonged irradiation a small shift in the isosbestic points is observed which is accompanied by deviations from linearity in the ED diagrams. After the irradiation is stopped the system reverts almost completely to the initial state obeying first-order kinetics (Fig. 1, curve 3). It follows from a more detailed analysis that the small deviation in the isosbestic behaviour of the spectra is due to an irreversible side reaction. By
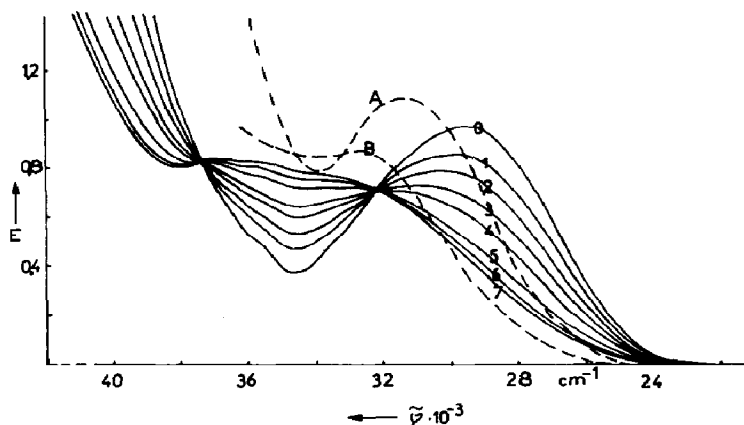
Fig. 1. Absorption spectra of DADA solutions in ethanol at various irradiation times (λ_{irrad} = 366 nm; θ = −56 °C; C_{DADA} = 3 × 10^{-4} M): curve 0, before irradiation; curve 1, 1 min; curve 2, 2 min; curve 3, 3.5 min; curve 4, 5 min; curve 5, 8 min; curve 6, 11 min; curve 7, 14 min; curve A, spectrum of α-methylbenzylidene aniline in dichloromethane before irradiation [6]; curve B, spectrum of α-methylbenzylidene aniline in dichloromethane extrapolated for the pure Z isomer [6].

analogy with the simple azomethines and azines the changes in the spectra are almost certainly due to $E \to Z$ isomerization. This assumption is supported by a comparison with the photochemical $E \to Z$ isomerization of α-methylbenzylidene aniline which is structurally related to one half of the DADA molecule [6] (see Fig. 1, curves A and B). In addition to the thermo-dynamically stable E,E isomer of DADA, the existence of the E,Z and the Z,Z forms should also be expected. However, the spectral changes produced on irradiation and the analysis of the kinetics of the dark reaction do not provide any evidence for the occurrence of the Z,Z isomer. The quantum yield Φ for the disappearance of the initial form was 0.08 in an air-saturated ethanol solution (λ_{irrad} = 366 nm; C = 2.4 × 10^{-4} M; θ = −50 °C). It was independent of the oxygen concentration of the solution indicating that direct photoisomerization proceeded from the S_1 state. The quantum yield is comparable with that obtained by Maeda and Fischer [6] for benzylidene aniline and its derivatives. The lack of dependence of the quantum yield on the oxygen content of the solution also agrees with the observations of Maeda and Fischer.

4. Kinetics of the thermal back reaction

The thermal back reaction that occurs following the irradiation of DADA in ethanol, ethylene glycol and methyl cyclohexane solutions was monitored in the temperature range −50 to −10 °C using a low temperature irradiation apparatus and in the temperature range 20 - 65 °C using a flash photolysis apparatus. The reaction obeys first-order kinetics. Figure 2 shows the temperature dependence of the rate constants and the activation parameters are given in Table 1. The results shown in Fig. 2 and Table 1 provide
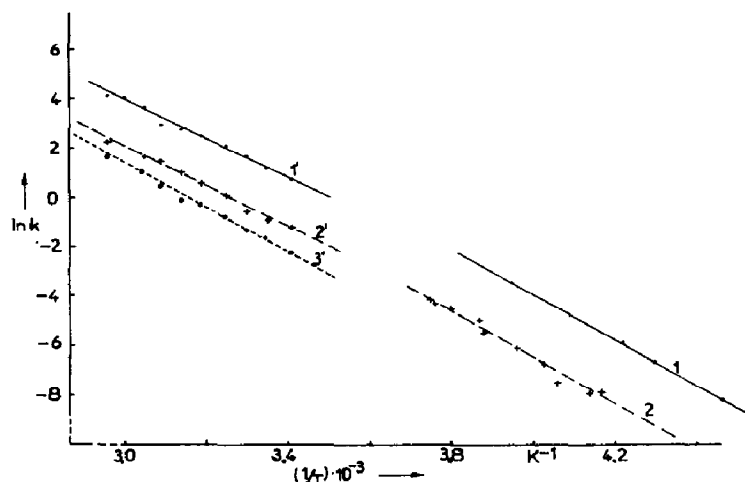
Fig. 2. Temperature dependence of the rate constants of the thermal reversion of DADA: curves 1 and 1', solutions in methyl cyclohexane; curves 2 and 2', solutions in ethanol; curve 3', solution in ethylene glycol.

TABLE 1

Activation parameters calculated from the temperature dependence of the $Z,E \rightarrow E,E$ isomerization of DADA

E_A (kJ mol^{-1})	log A	Temperature range (°C)	ΔS^* (J mol^{-1} K^{-1})	ΔG^* (kJ mol^{-1})	Solvent
63	11.6	20 - 65	—31 (20 °C)	70 (20 °C)	Methyl cyclohexane
68	11.6	20 - 65	—31 (20 °C)	75 (20 °C)	Ethanol
72	11.8	20 - 65	—27 (20 °C)	78 (20 °C)	Ethylene glycol
76	14.1	—50 to —10	18 (—20 °C)	69 (—20 °C)	Methyl cyclohexane
82	14.2	—50 to —10	20 (—20 °C)	75 (—20 °C)	Ethanol

evidence for a small temperature and solvent dependence of the activation parameters. The slightly higher values of E_A and log A obtained in the lower temperature region compared with the flash photolysis data are probably due to the increase in the viscosity of the solvent with decreasing temperature. The activation energies compare well with those obtained for benzylidene aniline and its derivatives for which a planar inversion mechanism has been demonstrated [10]. Activation energies of 100 kJ mol^{-1} have been determined for the $Z \rightarrow E$ isomerization of azines with higher condensed substituents [11]. The value of the pre-exponential factor A is typical of that for a monomolecular *cis* $\rightarrow$ *trans* isomerization; it is also of the same magnitude as that obtained for the isomerization of azines and azomethines. The slightly higher activation energy and free activation enthalpy obtained for the thermal back reaction in ethanol and ethylene glycol solutions is further evidence for a planar inversion mechanism. During the inversion a

transition state with sp hybridization is formed at the nitrogen atom. The possibility of π conjugation of the resulting lone p electron pair of nitrogen with the aryl π system leads to a decrease in the activation barrier. The initial form with sp^2 hybridization at the nitrogen atom shows a higher basicity than does the sp-hybridized transition state. Therefore the activation barrier should increase with increasing interaction of the solvent molecules with the lone pair at the nitrogen atom, *i.e.* if methyl cyclohexane is replaced by ethanol or ethylene glycol. An analogous discussion of the influence of the solvent and the substituent on the activation parameters of the $Z \to E$ isomerization has been given for benzylidene aniline [12].

5. Catalysis of the isomerization by acetic acid

Figure 3 shows the rate constants of the thermal back reaction of irradiated DADA as a function of the acetic acid concentration. Surprisingly, there is practically no dependence on acid concentration up to comparatively high values. Only at C_{Hac} values above 0.1 M does the rate constant increase with increasing acid concentration in an approximately quadratic manner. With the aromatic azines the substantially weaker benzoic acid causes a marked increase in the rate constant of the $Z \to E$ isomerization at concentrations as low as 10^{-3} M [11]. In contrast, the thermal $Z \to E$ isomerization of benzylidene aniline is inhibited in concentrated sulphuric acid by complete protonation of the lone electron pair of nitrogen at room temperature [13]. In order to explain the acceleration of the $Z \to E$ isomerization about C=N bonds by acids Jennings *et al.* [14] suggested that the acid anion adds by a reversible nucleophilic reaction to the double bond which is strongly polarized by protonation of the nitrogen atom. Thus the C=N bond
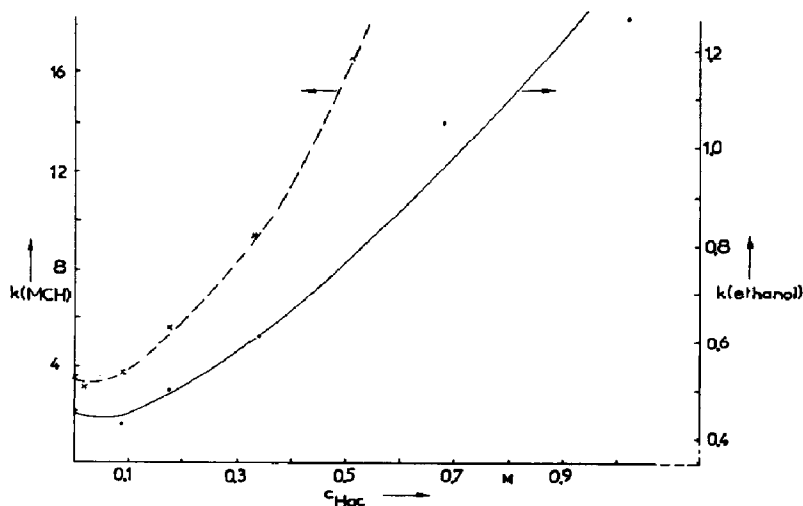

Fig. 3. Rate constants of the $Z \to E$ isomerization of DADA catalysed by acetic acid.

acquires a temporary single-bond character which allows it to rotate with a low activation barrier. If the rotation is rapid a very small fraction of protonated molecules is sufficient to accelerate the isomerization.

By analogy with simple azomethines the N-aryl-1,4-diazabutadienes should be twisted around the nitrogen—aryl bond. This allows the lone electron pairs of nitrogen to participate in the π conjugation of the aromatic rings. Twisting angles φ_E and φ_Z of about 55° and about 90° respectively have been reported for benzylidene aniline [15]. Such a conjugation of the lone electron pairs of nitrogen is impossible for the azines. Therefore the N-aryl-1,4-diazabutadienes should be weaker bases than the azines which explains the differences in the sensitivity towards acid catalysis.

Because of the different twists of the two nitrogen—aryl bonds in the photochemically generated E,Z isomer of DADA the molecule should exhibit two sites of different basicities. The site of the first protonation should preferably be the nitrogen atom in the E moiety, the lone pair of which is less delocalized because the nitrogen—aryl bond is less twisted. A distinct influence on the rate constants of the $Z \rightarrow E$ isomerization should of course only be observed if the interaction occurs with the lone pair in the Z moiety of the molecule which evidently applies only at higher acid concentrations. This gives a qualitative explanation of the non-linear catalysis plot shown in Fig. 3.

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