

A PHOTOACOUSTIC STUDY OF PHOTOCHROMIC REACTIONS IN THE CRYSTALLINE AND ADSORBED STATES[†]

H. GÜSTEN, G. HEINRICH and H. J. ACHE

Kernforschungszentrum Karlsruhe, Institut für Radiochemie, 7500 Karlsruhe (F.R.G.)

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Summary

The use of photoacoustic spectroscopy in the study of the absorption spectra and thermal kinetics of photochromic reactions in the crystalline and adsorbed states was demonstrated in the following photochemical reactions: *E*- α -(2,5-dimethyl-3-furylethylidene) (isopropylidene) succinic anhydride into 7,7a-dihydro-2,4,7,7a-pentamethyl-benzo[*b*]furan-5,6-dicarboxylic anhydride, 2-(2',4'-dinitrobenzyl)pyridine into its blue tautomeric form, bis-(2-*o*-chlorophenyl-4,5-*p*-methoxyphenyl)-diimidazolyl-1,1 into its stable free imidazolyl radical and *trans*-1,2-bis-[quinolinyl-(2)]-ethylidene dioxalate into its violene radical cation. By using the dual illumination technique the absorption spectra and thermal lifetimes of short-lived photochromic species can be recorded by means of photoacoustic spectroscopy.

1. Introduction

Parallel to the countless number of studies of photochemistry in the liquid or vapour phase, photochemical reactions in solid organic molecular crystals have also been investigated during the last 20 years [1, 2]. More recently, interest has increased in the photochemical reactions of organic molecules which are imposed by adsorption on a surface such as that of silica gel [3]. Organic molecules often change their spectroscopic and photochemical properties when adsorbed and immobilized on surfaces [4]. Common methods used for recording the spectroscopic properties of adsorbed molecules are diffuse reflectance spectroscopy or the immersion technique [4]. In the latter case the spectra and photochemistry of organic molecules adsorbed on silica gel immersed in an inert solvent have been investigated.

We describe here the use of photoacoustic (PA) spectroscopy in the study of the absorption spectra as well as the photochemical and thermal kinetics of some photochromic compounds in the crystalline and adsorbed

[†]Dedicated to Professor Dr. Dietrich Schulte-Frohlinde on the occasion of his 60th birthday.

states. There is a growing interest in solid state photochromic systems for various applications such as devices for computer memory elements, reusable information storage media or photomasking and photoresist technology. Some of the applications require that the photochromic process is reversible.

2. Experimental details

2.1. Instrumentation

The PA spectra of the photochromic compounds in the near-UV and visible ranges (250 - 800 nm) were measured using a single-beam home-made instrument which recorded them as a linear function of wavelength. The PA spectrometer is made up of the following components: a 450 W high pressure xenon lamp (XBO, Osram), a mechanical chopper (model 9479, Ortec-Brookdeal), a grating monochromator (model H25, I.S.A. Jobin-Yvon), a PA cell (model PAC 100, HMS-Elektronik) with a gas-coupled microphone (model PAD 30, HMS-Elektronik), a dual-filter preamplifier (model 4302, Ithaco) and a lock-in amplifier (model 5206, EG&G). The spectra can be recorded directly on an x - y recorder (BD 90, Kipp and Zonen) or processed using a desk-top computer (HP-86, Hewlett-Packard) equipped with a printer, a plotter and two floppy discs. This allows background correction, normalization and ratioing, to eliminate the dependence of the data on the spectral sensitivity of the xenon lamp and the monochromator, and subtraction of the sample spectrum to give that of the coloured photogenerated molecule. A second 450 W xenon lamp equipped with an elliptical reflector (model ALH 220, PRA) with optical feedback control (TX-5, PRA) was simultaneously used to study the PA spectra of short-lived photochromic compounds or intermediates. This set-up is shown in Fig. 1. Lamp 1 in combination with the UV reflecting mirror generates the photochromic species while the PA spectrum of the newly formed compound is measured by means of the modulated lamp 2. This is possible because the mirror in front of the PA cell is transparent in the visible spectral range (see the absorption-transmission curves in Fig. 1).

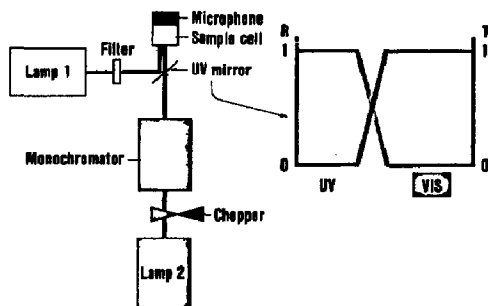


Fig. 1. Dual-lamp PA spectrometer for recording short-lived photochromic intermediates. The reflection R and the transmission T curves of the UV mirror are shown.

The light power of the xenon lamp-monochromator combination in the emission maximum at 470 nm (spectral bandwidth, 6 nm) at the location of the solid probe to be investigated is 1.5 mW. The sensitivity of the microphone in the frequency range 10 - 1000 Hz is approximately 10 mV Pa⁻¹ or 1 mV μ bar⁻¹. The detection limit of the signal from the amplifier of the microphone is approximately 1 μ V which corresponds to a pressure change of 10⁻⁴ Pa or 1 nbar.

Because of saturation phenomena of the PA signal of the photochromic compounds in the crystalline and adsorbed states the spectra were recorded with a chopping frequency of 1000 Hz.

2.2. Substances

E- α -(2,5-dimethyl-3-furylethylidene)(isopropylidene)succinic anhydride (compound A, Aberchrome 540; see Fig. 2(b)) was purchased from Aberchromics Ltd., and *trans*-1,2-bis-[quinolinyl-(2)]-ethylidene dioxalate and bis-(2-*o*-chlorophenyl-4,5-*p*-methoxyphenyl)-diimidazolyl-1,1 were supplied by our own laboratory. 2-(2',4'-dinitrobenzyl)pyridine and *N*-isopropyl-4-nitrothiobenzoimidate (I in Fig. 3) were kindly supplied by Dr. C. O. Meese. Silica gel 18 - 32 (Woelm G.m.b.H., Eschwege) with a particle size of 18 - 32 μ m and a surface area of 419 m² g⁻¹ was used for the adsorption of the photochromic compounds on active surfaces. The surface area was determined by means of the Brunauer-Emmett-Teller method using nitrogen.

The adsorption of the photochromic compounds on silica gel was performed by mixing the adsorbant and the adsorbate in a vibrating mill. The silica gel was dried at 200 °C overnight before use. The concentration of the adsorbed photochromic compounds investigated was generally in the range 5 \times 10⁻⁴ - 10⁻⁵ mol g⁻¹ silica gel to ensure monolayer coverage of the photochromic compounds.

3. Results and discussion

Breuer and Jacob [5] have shown the usefulness of PA spectroscopy in a study of the photoisomerization of thioindigo adsorbed on alumina. We have studied some well-known liquid phase photochromic reactions of organic compounds in the crystalline and adsorbed states.

The photochemical conversion of the pale yellow compound A into the red 7,7a-dihydro-2,4,7,7a-pentamethyl-benzo[*b*]furan-5,6-dicarboxylic anhydride (compound B) [6] occurs in the crystalline as well as the adsorbed state on silica gel and MgO. Figure 2(a) shows the recorded PA spectra of A, the sum of the recorded PA spectra of A and B, and the normalized difference PA spectrum of B which was computed by subtracting the PA spectrum of A from the coloured photogenerated A + B spectrum. The kinetics of the thermal back reaction of the B \rightarrow A reaction can also be monitored by PA spectroscopy. The exponential decay of the dark reaction B \rightarrow A was monitored at the absorption maximum of B (470 nm) on silica gel at room

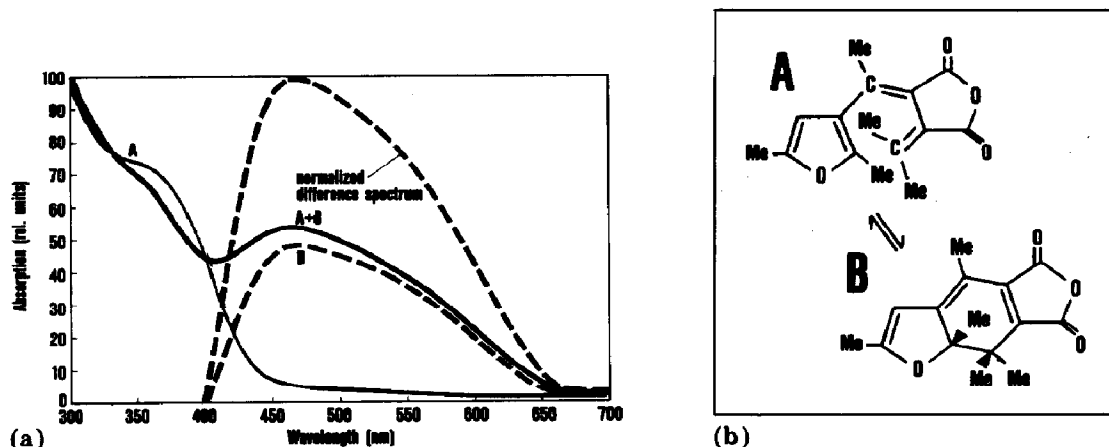
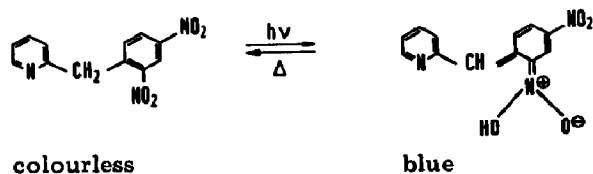


Fig. 2. The photochromic reaction of A to B adsorbed on silica gel measured using PA spectroscopy.

temperature. The thermal half-life of B at 24 °C depends on the concentration of A. In the concentration range $7.5 \times 10^{-4} - 3 \times 10^{-5} \text{ mol g}^{-1}$ on silica gel the thermal half-life of B increases from 49 to 196 min. At all concentrations studied the thermal back reaction follows an exponential decay. Since B is also converted photochemically to A the modulated light of the PA spectrometer is used for a few seconds only during the thermal kinetics runs to monitor the intensity of the PA signal at a given time. The photochromic system A \rightarrow B (see Fig. 2(b)) has been proposed as a chemical actinometer in solution [6]. We have used compound A adsorbed on silica gel as a relative actinometer to control the incident light intensity of a photoreactor between 300 and 400 nm for the study of heterogeneous photochemical reactions in the adsorbed state [7]. Since the photochromic reaction on silica gel is not completely reversible, however, compound A cannot be recommended as a reusable chemical actinometer in the adsorbed state. With white light the coloured form is not completely reversed to A. A permanent faint orange-brown colour remains on the surface of the silica gel after the photochromic reaction.

In the same manner, the absorption spectra of the photochromic reaction of the colourless 2-(2',4'-dinitrobenzyl)pyridine into its blue tautomeric form in the crystalline and adsorbed states on silica gel



were recorded by PA spectroscopy. The thermal back reaction was monitored at the absorption maximum of 620 nm. At a concentration of $5 \times 10^{-5} \text{ mol}$

g^{-1} on silica gel the half-life of the blue tautomeric form at room temperature was 160 min.

It has been demonstrated previously by electron spin resonance spectroscopy that some organic photochromic systems generate fairly stable free radicals in the solid state [8, 9]. The slow solid state thermal reaction of the photogenerated blue free imidazolyl radical to its pale yellow parent compound bis-(2-*o*-chlorophenyl-4,5-*p*-methoxyphenyl)-diimidazolyl-1,1 at 24 °C was measured by PA spectroscopy at the absorption maximum of the photogenerated blue radical at 600 nm. The kinetics of the thermal back reaction of the free imidazolyl radical in the adsorbed state on silica gel depend on the concentration. The same result was found for the thermal reaction of the phototropic black violene radical cation of *trans*-1,2-bis-[quinolinyl-(2)]-ethylidene dioxalate adsorbed on silica gel [9]. The absorption maximum of the violene radical cation on silica gel is at 520 nm compared with 545 nm in ethanol. Since the absorption spectrum of the violene radical cation in the solid and adsorbed states extends far into the near-IR, the colour appears black. While the thermal half-life of the photogenerated violene at 20 °C in ethanol is less than 1 s [9], the thermal half-life in the adsorbed state on silica gel is of the order of 10 h.

With the dual illumination technique it can be further demonstrated that the absorption spectra and thermal lifetimes of short-lived photochromic species can also be recorded by PA spectroscopy. The white crystals of *N*-isopropyl-4-nitrothiobenzoimide turn blue ($\lambda_{\max} = 620$ nm) under near-UV irradiation. Lamp 1 in combination with the UV mirror (see Fig. 1) generates the blue colour with light of wavelengths from 300 to 400 nm while the PA spectrum (Fig. 3) is recorded by means of the modulated lamp 2 over the entire visible wavelength range. When lamp 1 is switched off the blue colour fades in the dark with a half-life of 4.5 s at 26 °C. Figure 4 shows the exponential decay of the thermal reaction of the blue-coloured species measured by PA spectroscopy at the absorption maximum at 620 nm as a

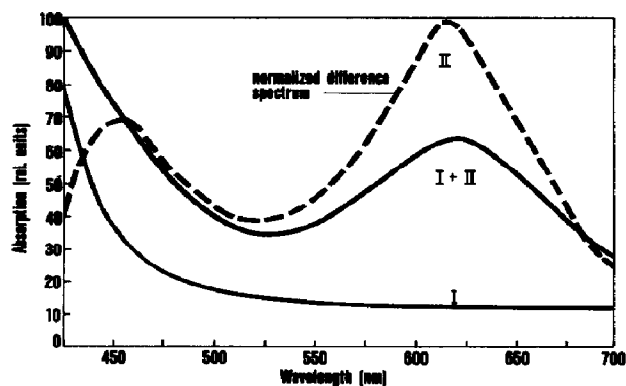


Fig. 3. The photogeneration of a blue-coloured compound (II) from crystalline *N*-isopropyl-4-nitrothiobenzoimide (I) measured by means of PA spectroscopy using the dual illumination technique.

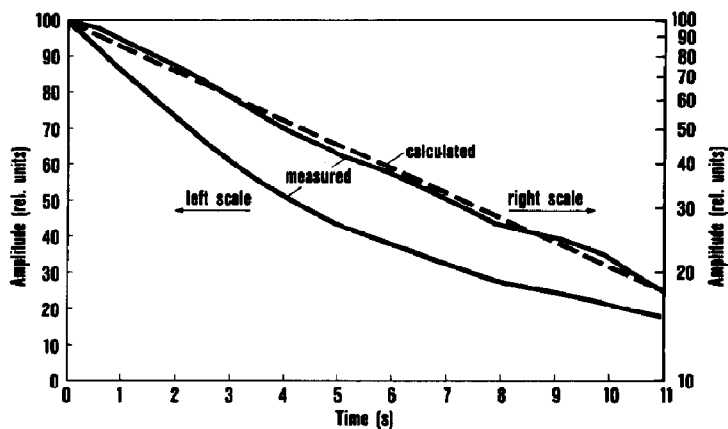


Fig. 4. Kinetics of the thermal fading of the blue-coloured compound of Fig. 3 measured by means of PA spectroscopy at room temperature.

direct recording of the PA signal on the x - y recorder on a normal scale together with a logarithmic plot generated by the computer. In contrast with the other photochromic reactions described here, phototropy of *N*-isopropyl-4-nitrothiobenzoimidate does not occur in the adsorbed state on silica gel or MgO. Details of the molecular structure of the blue photochromic product will be reported elsewhere [10].

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