

## REFLECTANCE SPECTROSCOPY FOR THE CHARACTERIZATION OF PHOTOCHROMISM IN THE CRYSTALLINE STATE

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**Abstract**—The Kubelka–Munk theory for diffuse reflectance has been applied to a quantitative study of photochromism in the crystalline state. For three systems investigated it was found possible to assign first order rate constants to the thermal relaxation process and estimate the pre-exponential factor  $A$  and the activation energy  $E_a$  in Arrhenius equation. For the fading of the red photocolored form,  $\lambda_{max}=490\text{ m}\mu$ , of benzaldehyde phenylhydrazone  $A=1.4 \times 10^8\text{ min}^{-1}$  and  $E_a=15.7\text{ kcal mole}^{-1}$ . For the fading of the blue photocolored form,  $\lambda_{max}=590\text{ m}\mu$ , of 2-(2,4-dinitrobenzyl)pyridine  $A=5 \times 10^{14}\text{ min}^{-1}$ ,  $E_a=23.3\text{ kcal mole}^{-1}$ . Cinnamaldehyde semicarbazone showing 'reversed phototropy' has a photoactivated state,  $\lambda_{max}=400\text{ m}\mu$ , which in dark is transformed into a strongly absorbing yellow species,  $\lambda_{max}=430\text{ m}\mu$  with  $A=1.4 \times 10^{10}\text{ min}^{-1}$  and  $E_a=18.7\text{ kcal mole}^{-1}$ .

### INTRODUCTION

THE PROCESS of photochromism has been observed with a great variety of substances.<sup>(1)</sup> In particular it is known that colorless crystals of benzaldehyde phenylhydrazone reddens when they are exposed to light and that the red color fades in the dark.<sup>(2)</sup> Another, often studied, photochromic compound is 2-(2,4-dinitrobenzyl)pyridine, where the colorless crystals turn deeply blue when irradiated but return to colorless in the dark over a period of a day at room temperature.<sup>(9)</sup>

Cinnamaldehyde semicarbazone exhibits a type of photochromism which is the converse of that ordinarily observed.<sup>(10)</sup> When first prepared it is colorless, and if immediately placed in the dark, it remains colorless and undergoes no further change. If the semicarbazone is exposed to diffuse sunlight for some hours no visible effect is noticeable but thereafter in the dark, a yellow color develops on the irradiated surfaces. The yellow color disappears on re-exposure of the sample to light and is restored in the dark. The cycle can be repeated several times and it is also reported that recrystallization of the yellow or the active colorless form yields back the original colorless inactive modification. The name 'reversed phototropy' has been applied to this type of behavior.<sup>(3)</sup>

### GENERAL THEORY AND APPROACH

Kubelka and Munk<sup>(6,7)</sup> have developed a general theory for diffuse reflectance spectroscopy. The experimental validity of this theory has been investigated in particular by

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Kortum and co-workers<sup>(5)</sup> who employed the Kubelka-Munk equation:

$$F(R_\infty) \equiv \frac{(1-R_\infty)^2}{2 R_\infty} = \frac{\mathcal{K}}{s} \quad (1)$$

$R_\infty$  denotes the relative diffuse reflectance with reference to a nonabsorbing white standard, i.e. the ratio between the intensities of the diffusely reflected beams from the sample and the standard, respectively.  $\mathcal{K}$  is the absorption coefficient and  $s$  the scattering coefficient. Common standards used in the determination of the quantity  $R_\infty$  include magnesium oxide, barium sulfate and sodium chloride.  $R_\infty$  refers to infinite thickness of the layer but it is found in practice that an increase in sample thickness above a few millimeters causes no observable change in the intensity of the diffusely reflected beam. The contribution of regular reflectance to the total reflectance decreases with decrease in particle size. The true reflectance spectrum is commonly obtained by decrease in particle size brought about by extensive milling. It is indicated that for a moderately absorbing substance a grain size below about  $1\mu$  usually ensures a negligible contribution from regular reflectance.

Excellent results have been obtained for the reflectance spectra of adsorbed substances when the adsorbent is used as the reflectance standard<sup>(5)</sup> making it possible to ensure very similar particle size distributions for sample and reference. The experimental measurements suggest that it is reasonable to assume that  $s$  is independent of wavelength in the ultraviolet and visible. It is also possible at sufficiently low concentration of adsorbate to employ the equation

$$\log_{10} F(R_\infty) = \log_{10} C + \log_{10} \epsilon + \text{constant} \quad (2)$$

obtained by substituting  $\epsilon C$  for  $\mathcal{K}$  in equation (1).  $\epsilon$  designates molar extinction coefficient of adsorbate and  $C$  its concentration. Kortum, *et al.*, have found that the kinetics of the reversible photochromic behavior of 2-(2,4-dinitrobenzyl)pyridine can be studied using the pure adsorbent as the reference standard.<sup>(4)</sup>

We report here the application of equation (2) to the crystalline powders of the photochromic substances benzaldehyde phenylhydrazone, 2-(2,4-dinitrobenzyl)pyridine and cinnamaldehyde semicarbazone, using as reflectance standard, the unexposed nonabsorbing photosensitive form. ( $C$  and  $\epsilon$  stand in this case for concentration and extinction coefficient of photocolored material). For a given concentration of formed photocolored substance plots of  $\log_{10} F(R_\infty)$  versus wavelength yield absorption spectra in terms of  $\log_{10} \epsilon$  which are displaced a constant value along the  $\log_{10} \epsilon$  - axis. Conversely at any selected wavelength  $\log_{10} F(R_\infty)$  is a measure of  $\log_{10} C$  less a constant; hence if the color is fading in a first order reaction a plot of  $\log_{10} F(R_\infty)$  versus time,  $t$ , gives a straight line

$$\log_{10} F(R_\infty) = -(\log_{10} e) kt + \text{constant} \quad (3a)$$

$k$  being the rate constant. In case the light absorbing, colored substance is being formed, the equation is

$$\log_{10} [F_\infty(R_\infty) - F(R_\infty)] = -(\log_{10} e) kt + \text{constant} \quad (3b)$$

$F_\infty(R_\infty)$  denotes the value of the Kubelka-Munk function (1) after completion of the reaction.

## RESULTS AND DISCUSSION

### *Benzaldehyde phenylhydrazone and 2-(2,4-dinitrobenzyl)pyridine*

Unirradiated samples of benzaldehyde phenylhydrazone and 2-(2,4-dinitrobenzyl)pyridine show essentially no absorption in the visible and were kept as standards for reflectance measurements in this region of the spectrum.

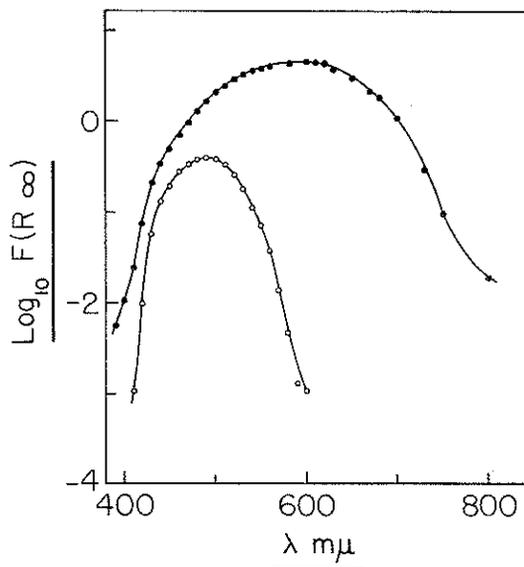


FIG. 1. Reflectance spectra after 2 min exposure to u.v. light of:

- benzaldehyde phenylhydrazone.
  - 2-(2,4-dinitrobenzyl)pyridine.
- The samples were kept at 20.8°C.

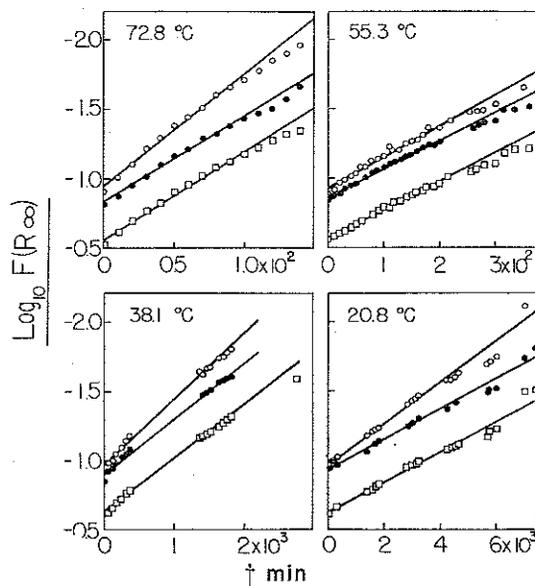


FIG. 2. Kinetic plot, using equation (3a), for the fading of photocolored benzaldehyde phenylhydrazone at four temperatures and monitored at three wavelengths. From the slopes the following first order rate constants were obtained:

Monitoring Wavelength mμ	Symbol	Temperature			
		20.8	38.1	55.3	72.8°C
		$k \times 10^4$	$k \times 10^3$	$k \times 10^3$	$k \times 10^2 \text{ min}^{-1}$
530	○	3.4	1.10	5.6	1.9
450	●	2.5	0.96	4.9	1.4
490	□	2.5	0.87	4.9	1.5

Samples exposed to u.v. light gave the spectra shown in Fig. 1. An absorption band with maximum at  $490\text{ m}\mu$  gave the sample of benzaldehyde phenylhydrazone the red color. The blue color of 2-(2,4-dinitrobenzyl)pyridine corresponded to a broad band with maximum at  $590\text{ m}\mu$ . In the dark these absorption bands gradually disappeared and the reflectance of the samples returned to the state before exposure. It is shown in Figs. 2 and 3 that this thermal fading can be fairly accurately described by equation (3a). The data in the figures refer to measurements on a fresh sample for each temperature after irradiation

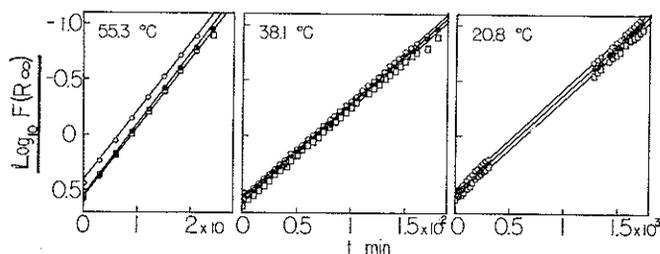


Fig. 3. Kinetic plot, using equation (3a), for the fading of photocolored 2-(2,4-dinitrobenzyl)pyridine at three temperatures and monitored at three wavelengths ( $\circ=600\text{ m}\mu$ ,  $\bullet=570\text{ m}\mu$ ,  $\square=630\text{ m}\mu$ ). From the slopes the following first order rate constants in  $\text{min}^{-1}$  were obtained:  $2.1 \times 10^{-3}$  ( $20.8^\circ\text{C}$ ),  $2.0 \times 10^{-2}$  ( $38.1^\circ\text{C}$ ) and  $1.4 \times 10^{-1}$  ( $55.3^\circ\text{C}$ ). Identical rate constants were obtained at all three wavelengths.

for 2 min with u.v. light. Re-exposure of a sample gave identical kinetics within experimental errors. After repeated cycling a permanent absorption change became noticeable and the photochromic response diminished.

Arrhenius plots of the rate constants obtained from Figs. 2 and 3 are presented in Fig. 4 and the rate parameters  $A$  and  $E_a$  in Arrhenius equation  $k=A \exp(-E_a/RT)$  together with the rate constants at  $20.8^\circ\text{C}$  are collected in Table 1. These data were determined from the mean values of the rate constants obtained by monitoring at different wavelengths,

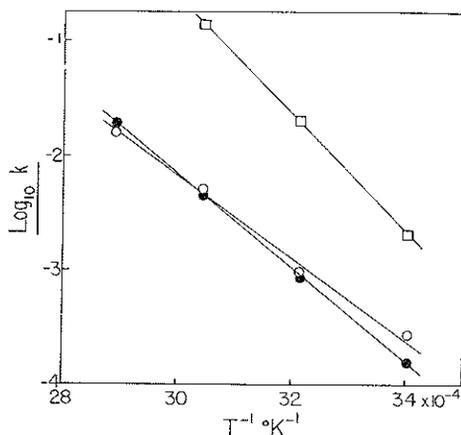


FIG. 4. Arrhenius plots using the mean values of the rate constants obtained from Figs. 2, 3 and 6.

- $\circ$  benzaldehyde phenylhydrazone.
- $\square$  2-(2,4-dinitrobenzyl)pyridine.
- $\bullet$  cinnamaldehyde semicarbazone.

TABLE 1. RATE PARAMETERS, FOR THE FADING OF PHOTOCOLORED CRYSTALS OF BENZALDEHYDE PHENYLHYDRAZONE AND 2-(2,4-DINITROBENZYL)PYRIDINE, AND FOR THE REACTION  $\beta \rightarrow \gamma$  OF CINNAMALDEHYDE SEMICARBAZONE.

Compound	$k$ (20.8°C) (min <sup>-1</sup> )	$A$ (min <sup>-1</sup> )	$E_a$ (kcal mole <sup>-1</sup> )
Benzaldehyde phenylhydrazone	$2.8 \times 10^{-4}$	$1.4 \times 10^8$	15.7
2-(2,4-dinitrobenzyl) pyridine	$2.1 \times 10^{-3}$	$5 \times 10^{14}$	23.3
Cinnamaldehyde semicarbazone	$1.6 \times 10^{-4}$	$1.4 \times 10^{10}$	18.7

Figures 2 and 3. It should be noted that the activation energy for 2-(2,4-dinitrobenzyl)pyridine in Table 1 is considerably higher than the 15–17 kcal mole<sup>-1</sup> Kortum, *et al.*<sup>(4)</sup> obtained for the photochromism of this compound in the adsorbed state.

#### Cinnamaldehyde semicarbazone

In ethanol solution cinnamaldehyde semicarbazone shows no absorption in the wavelength interval 380–600 m $\mu$  and it was accordingly attempted to use the unexposed sample as reflectance standard in this interval.

The reflectance spectrum of a sample of cinnamaldehyde semicarbazone taken immediately after exposure to u.v. light showed a fairly well-defined peak at a wavelength of 400 m $\mu$ , cf. Fig. 5. On standing in the dark, the material became yellow and displayed a broad absorption band with a maximum at 430 m $\mu$ . This yellow material

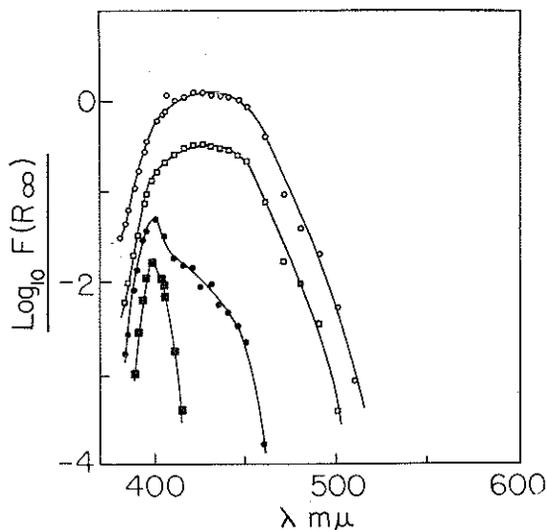


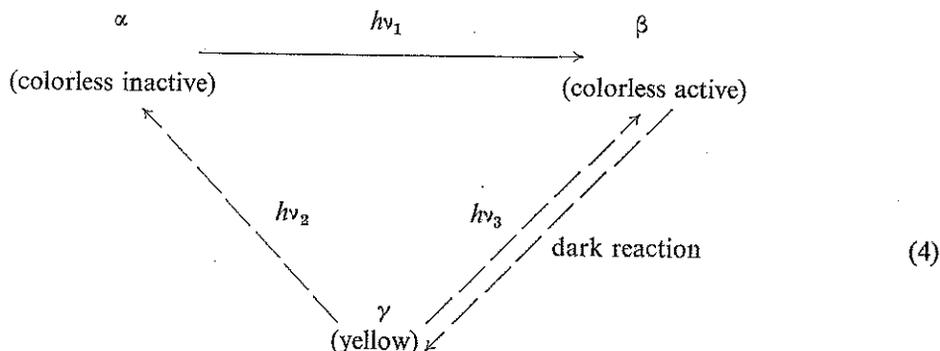
FIG. 5. Reflectance spectra of cinnamaldehyde semicarbazone.

- immediately after 2 min exposure to ultraviolet light (species  $\beta$  with small amount of  $\gamma$ ).
- same sample after standing in darkness for 8 days to complete reaction  $\beta \rightarrow \gamma$  (species  $\gamma$ ).
- same sample after reirradiation, this time with visible light, 60 min (species  $\beta$ ).
- same sample after standing in darkness for 8 days to complete reaction  $\beta \rightarrow \gamma$  (species  $\gamma$ ).

The sample was kept at 38.1°C.

turned white again on exposure to visible light (light from fluorescent laboratory lamps or daylight), yielding a spectrum similar to the one first obtained. The intensity of the 400  $m\mu$  band was, however, notably reduced. On standing in the dark, the sample again turned yellow but with lesser intensity of the color, the 430  $m\mu$  band being reduced to about the same extent as the 400  $m\mu$  band for the preceding unstable colorless modification.

The reflectance measurements on cinnamaldehyde semicarbazone verified the existence of the three species,  $\alpha$ ,  $\beta$  and  $\gamma$  related according to the reaction pattern below.



The scheme is basically the same as the one brought forward by Heilbron *et al.*<sup>(3,10)</sup>

$\alpha$  reacts on exposure to ultraviolet light to form  $\beta$  having increased absorption at around 400  $m\mu$ .  $\beta$  thermally transforms into  $\gamma$  which absorbs at wavelengths around 430  $m\mu$ . The photochemical production of  $\beta$  from  $\gamma$  by means of visible light was also evidenced, but it was observed that, although visible light caused all  $\gamma$  present to disappear,  $\gamma$  was then not quantitatively transferred into  $\beta$ . The following experiment suggests that this might be due to a partial reformation of  $\alpha$  by the visible light:

$\alpha$  was illuminated with the ultraviolet lamp until there was no further increase in  $\beta$ , subsequently the yellow form was allowed to develop in the dark. Next, the yellow form was exposed to the ultraviolet lamp whereupon  $\beta$  was essentially quantitatively regained. The system can so be recycled between  $\beta$  and  $\gamma$  several times without noticeable decrease in the intensity of the absorption of  $\beta$  and  $\gamma$ .

The experiments do not allow us to exclude the possibility that any of the photochemical reactions in the scheme involves the third component (of the scheme) as an intermediate.

$\alpha$  was illuminated with ultraviolet light until no further increase in amount of  $\beta$  was noticeable as monitored at 400  $m\mu$ . The reaction  $\beta \rightarrow \gamma$  was followed as a function of time at four wave lengths (400, 420, 440 and 450  $m\mu$ ). The rate constant for this transition was determined from plots of  $\log_{10} [F_{\infty}(R_{\infty}) - F(R_{\infty})]$  versus time as shown in Fig. 6. A linear dependence was obtained for the investigated region. It was also found that a tenfold increase in exposure time over the time needed to completely convert  $\alpha$  into  $\beta$  caused no significant changes in the rate  $\beta \rightarrow \gamma$ . At 38.1°C, for 1 and 10 min exposure, the value of the rate constants obtained from the slopes of the lines of  $\log_{10} [F_{\infty}(R_{\infty}) - F(R_{\infty})]$  versus time at 420  $m\mu$  were  $8.6 \times 10^{-4} \text{ min}^{-1}$  and  $1.10 \times 10^{-3} \text{ min}^{-1}$ , respectively. The data in Fig. 6 were obtained from samples exposed for 2 min to the u.v. light. It is noted that monitoring at different wavelengths and application of equation (3b) yield essentially the same rate parameters. It should be noticed that at 400  $m\mu$  both  $\beta$  and  $\gamma$  absorb.

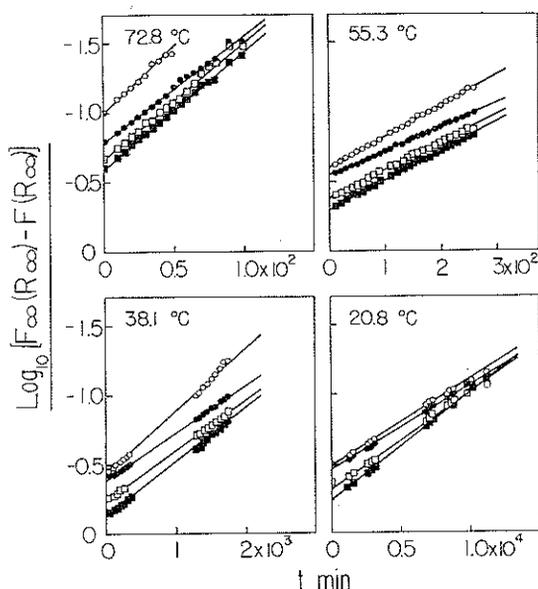


FIG. 6. Kinetic plot, using equation (3b), for the reaction  $\beta \rightarrow \gamma$  at four temperatures and monitored at four wavelengths. From the slopes the following first order rate constants were obtained.

Monitoring Wavelength m $\mu$	Symbol	Temperature			
		20.8 $k \times 10^4$	38.1 $k \times 10^4$	55.3 $k \times 10^3$	72.8°C $k \times 10^2 \text{ min}^{-1}$
400	○	1.5	10.3	5.0	2.2
450	●	1.4	7.7	3.9	1.7
440	□	1.7	8.1	4.2	1.9
420	■	1.8	8.8	4.8	1.9

Using the rate constants,  $k$ , obtained from the slopes of the straight lines in Fig. 6, Arrhenius plots were drawn with data for the four temperatures, Fig. 4. The parameters in the equation  $k = A \exp(-E_a/RT)$  are presented in Table 1.

#### EXPERIMENTAL

Benzaldehyde phenylhydrazone (Eastman Organic Chemicals) was recrystallized from ethanol m.p. 156°C.

2-(2,4-Dinitrobenzyl)pyridine was synthesized by Frank H. Bissett of these laboratories. It was purified through repeated recrystallization from ethanol, m.p. 93°C.

Cinnamaldehyde semicarbazone was prepared according to Shriner, *et al.*,<sup>(6)</sup> Yellowish crystals of impure semicarbazone yielded white crystals with m.p. 215°C after five recrystallizations from absolute ethanol. Chemicals used were: Cinnamaldehyde (chlorine-free) Eastman Organic Chemicals; Semicarbazide Hydrochloride, Fisher Scientific Company; Sodium Acetate (anhydrous), Baker and Adamson; Ethanol (absolute), USP.

Vacuum dried samples were milled in the dark with porcelain balls for 16 hr. The milled powder was placed in two brass cells; the material was packed gently and covered with a quartz disc. The brass cells were kept at constant temperature by circulating water from a constant temperature bath through an outer jacket. A Zeiss spectrophotometer

PMQ II with reflectance attachment RA2 was used for the reflectance measurements. One cell was irradiated and the subsequent spectral changes were measured with the un-irradiated sample as reference.

Ultraviolet light was obtained from an air-cooled high pressure mercury lamp, Hanovia 612C, operated at 400 W, the sample surface kept 13 cm from the surface of the lamp.

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