PHOTOCHROMISM AND THERMOCHROMISM OF DITHIZONE IN SOLUTION

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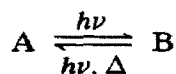
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Summary

Dithizone behaves as a photochromic

$$A \underset{h\nu, \Delta}{\overset{h\nu}{\rightleftharpoons}} B$$

system (green $\rightleftharpoons$ red) in pure hexane; in acetone and acetonitrile a second transient is observed. As proved by the kinetic deuterium isotope effect and base catalysis of the thermal reverse reaction the photochromism is interpreted in terms of tautomeric and geometric transformations. A proposal is presented for a possible structural assignment of the phototransients.

1. Introduction

The photochromic behaviour of primary metal dithizonates in solution has been investigated for about 40 years; the first comprehensive results were reported by Meriwether and coworkers [1, 2] who detected photochromism with nine primary dithizonates out of a total of 24 complexes investigated. The kinetics of the photochromic reactions [3 - 6] and the structure of the photoisomer [7, 8], with particular emphasis on mercury(II) dithizonate, were the main subjects of later papers. With regard to a potential technical interest Dahlberg and Reinganum [9] investigated for the first time the photochromism of zinc dithizonate in the solid state and they reported coupling between its photochromic and its electronic properties.

The photochromic behaviour of S-methyl dithizone has similarly been well investigated [10 - 12]. Much attention has been paid to this derivative of dithizone in particular regarding the elucidation of the structural nature of dithizone itself [13].

Meriwether and coworkers [1, 2] have, incidentally, referred to the expected photochromic properties of the parent compound dithizone

(3-mercapto-1,5-diphenylformazan). Later, Coleman *et al.* [14] tried to measure the spectrum of the metastable photochromic form of dithizone.

In contrast with the opinion prevailing for about 100 years, according to which an equilibrium of two tautomeric forms I $\rightleftharpoons$ II

$$PhNH—NH—\underset{\underset{S}{\|}}{C}—N=NPh \qquad PhNH—N=\underset{\underset{SH}{|}}{C}—N=NPh$$
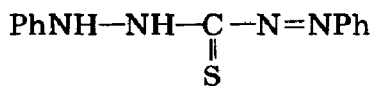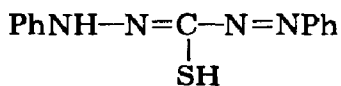
I   II

is responsible for the two absorption bands of dithizone in organic solvents, it is now well established that dithizone exists as a single species under these conditions [13, 15]. Such solutions are green at room temperature as a result of distinct absorption maxima at $\lambda_{max\,1} \approx 600$ nm and $\lambda_{max\,2} \approx 450$ nm, the intensity ratio $R = \epsilon_{max\,1}/\epsilon_{max\,2}$ of which being typical for the particular solvent. We have recently interpreted the dependence of the spectra on the nature of the solvent in terms of solvatochromism [16].

We have dealt with the thermochromic and photochromic behaviour of dithizone [17 - 19] which has arisen from the elucidation of some problems in the application of dithizone in trace analysis [20], and we wish to present our results in this paper.

2. Experimental details

All solutions of dithizone in the thoroughly purified solvents *n*-hexane, acetone and acetonitrile were freshly prepared under the exclusion of actinic light. The samples for ordinary spectroscopic measurements were stirred during the irradiation and recording periods. The irradiation wavelengths were selected by interference filters. The light intensities were determined by means of a ferrioxalate actinometer or with the help of thioindigo or perinaphthioindigo as secondary actinometers. The flash photolysis apparatus applied was of a conventional design. Cut-off filters (Schott OG 2 ($\lambda \geqslant$ 550 nm); GA 50 ($\lambda \geqslant$ 500 nm)) and bandpass filters (BG 7 (λ_{max} = 480 nm)) were used for the flash excitation. For further experimental details the reader is referred to ref. 21.

3. Results

3.1. Photochromism in n-hexane

In *n*-hexane dithizone behaves as a photochromic

$$A(green) \underset{h\nu,\,\Delta}{\overset{h\nu}{\rightleftharpoons}} B(red)$$
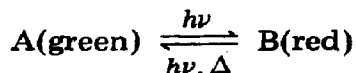
system (see ref. 17). The lifetime of B is 0.42 ± 0.1 s at 25 °C (mean value from 27 shots in the region 430 - 700 nm). At −70 °C the photochromic behaviour could be studied without interference from thermal reactions. Figure 1 shows the spectra recorded at −70 °C after irradiation with light of wavelengths $\lambda_1' = 546$ nm and $\lambda_2' = 436$ nm in addition to the absorption spectrum of the original form A. On the assumption that only A absorbs at wavelengths $\lambda \geqslant 680$ nm which seems to be well justified a conversion ratio α of 0.5 is calculated for the photostationary state obtained on irradiation with $\lambda' = 436$ nm. From this value the spectrum of the photochromic form B can be calculated (Fig. 1, curve 4). In flash experiments conversion ratios of about 0.95 and 0.85 were observed on exciting the first (550 nm cut-off filter) or second (480 nm cut-off filter) transition respectively, whereas a conversion ratio of only about 0.45 was obtained with a 500 nm cut-off filter. This again proves the photoreversibility of the photochromic reaction. The phototransformation

$$A \xrightarrow{h\nu} B$$
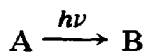
is monophotonic as shown by the linear dependence of the reversible extinction change obtained per flash on the flash intensity.
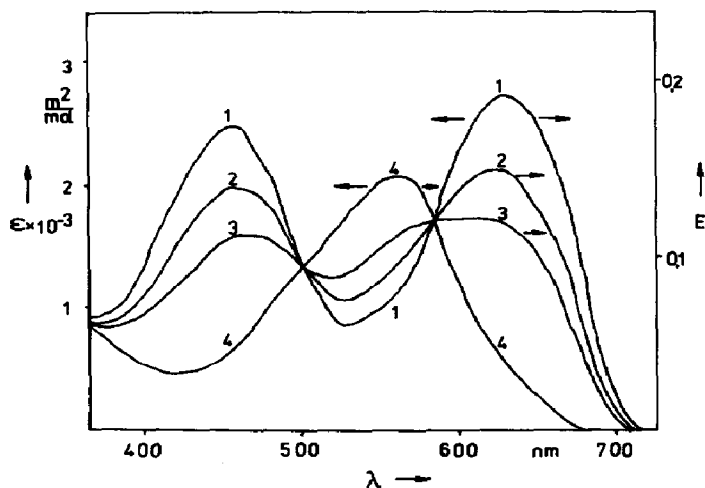

Fig. 1. Absorption spectra of dithizone (7×10^{-6} M) in hexane at −70 °C (supersaturated): curve 1, form A; curve 2, photostationary state obtained from irradiation with $\lambda' = 436$ nm; curve 3, photostationary state obtained from irradiation with $\lambda' = 546$ nm; curve 4, calculated spectrum of form B.

The thermal reversion is a unitary reaction as can be readily seen from the linear extinction difference (ED) diagrams obtained from the difference spectra of the flash experiments (Fig. 2). It strictly obeys first-order kinetics. The rate constants are independent of the detection wavelength. From the Arrhenius plot (Fig. 3) an activation energy $E_A = 48.1 \pm 1.6$ kJ mol^{-1} and a pre-exponential factor $\lg A = 8.9 \pm 0.3$ were obtained. Using the Eyring
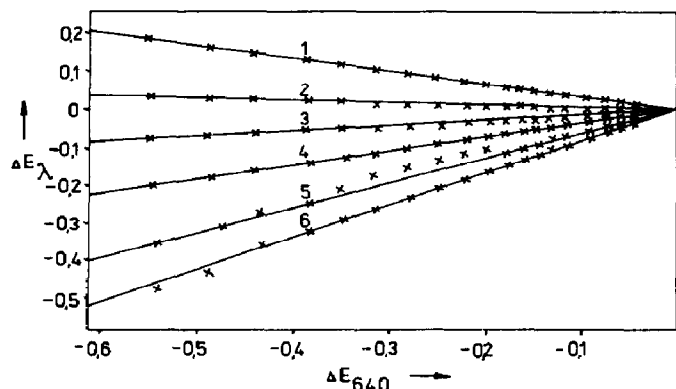
Fig. 2. ED diagrams for the thermal back reaction of flashed dithizone in hexane: curve 1, $\lambda = 520$ nm; curve 2, $\lambda = 500$ nm; curve 3, $\lambda = 580$ nm; curve 4, $\lambda = 480$ nm; curve 5, $\lambda = 440$ nm; curve 6, $\lambda = 620$ nm.
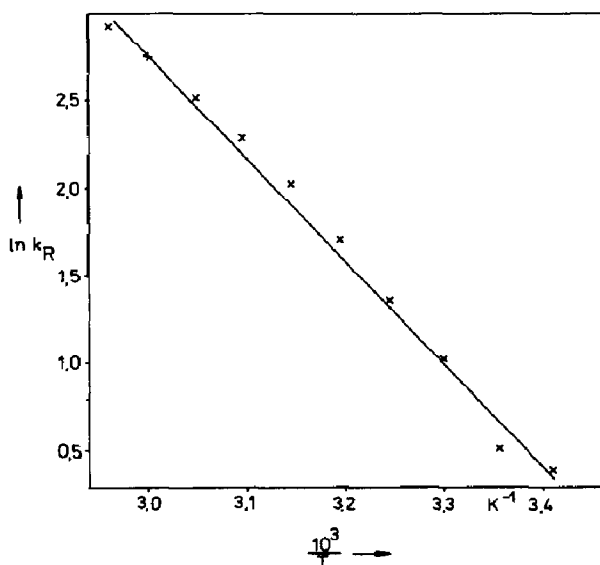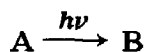

Fig. 3. Arrhenius plot for the thermal back reaction of form B in hexane ($\lambda = 530$ nm).

equation this results in $\Delta H^{\ddagger} = 45.6$ kJ mol^{-1}, $\Delta S^{\ddagger} = -82.3$ J mol^{-1} K^{-1} and $\Delta G^{\ddagger} = 70.3$ kJ mol^{-1}.

For the quantum yield φ of the photoreaction

$$A \xrightarrow{h\nu} B$$

we obtained a rough estimate of about 0.2 which should be regarded as a lower limit (see ref. 17). The exact determination of the quantum yields for the forward and reverse photoreactions failed because of crystallization of the solute from the supersaturated solutions at low temperature.

To obtain some information about the nature of the phototransient and the dark reaction especially whether protolytic or tautomerization reactions

were involved we have studied acid–base catalysis of the reaction, transient conductivity changes and the deuterium isotope effect.

The thermal reverse reaction can be catalysed by organic bases but not by weak acids, *e.g.* acetic acid. The observed pseudo-first-order rate constants were found to be strictly proportional to the concentration of the bases present over two orders of magnitude or more (base concentrations in the range 5×10^{-5} - 2×10^{-2} M depending on the strength of the particular base). The catalysis constants were obtained from the slopes of the regression lines k_{obs} *versus* the base concentration. In all cases the ordinary absorption spectra were identical with that of the dithizone solution, thus excluding any ground state interaction or equilibrium with the bases within the concentration range used.

Figure 4 shows the Brønsted plot for the bases piperidine, ethylamine, benzylamine, *sym*-collidine, γ-picoline, pyridine and *N*-methylaniline. For the right leg of the correlation the Brønsted coefficient β is 0.91.
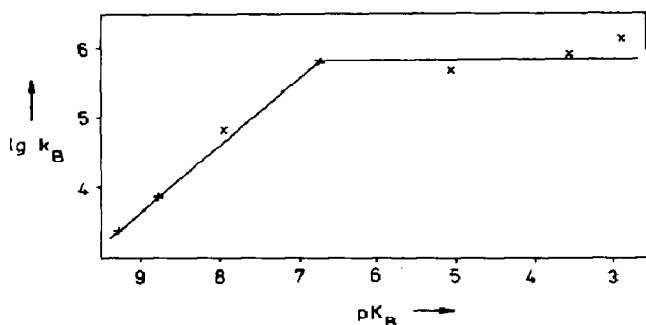

Fig. 4. Brønsted plot for the base-catalysed reverse reaction B → A of dithizone in *n*-hexane.

Parallel to the optical detection we observed a small but significant transient decrease in the conductivity on flash excitation (in acetonitrile). It follows unequivocally from this observation that the photochromic form B must not be mistaken for the monoanion of dithizone which also shows a red colour [18].

With dithizone-d_2 we were able to measure a primary kinetic deuterium isotope effect k_H/k_D of 5.5 ± 0.1 for the thermal reversion B → A in hexane. Deuteration of dithizone was performed simply by shaking the hexane solutions with D_2O. The reference sample was treated in the same manner with H_2O. It did not show a significant change in the rate constants compared with the dry solution. Interestingly, the same isotope effect was obtained for the base catalysis constant with piperidine.

3.2. Photochromism in acetone and acetonitrile

Figure 5 shows the transient spectra of a solution of dithizone in acetone obtained on flash irradiation at room temperature. It can be clearly seen that in the first period of the relaxation the absorption of species B around 520 nm vanishes without a substantial recovery of the absorption of
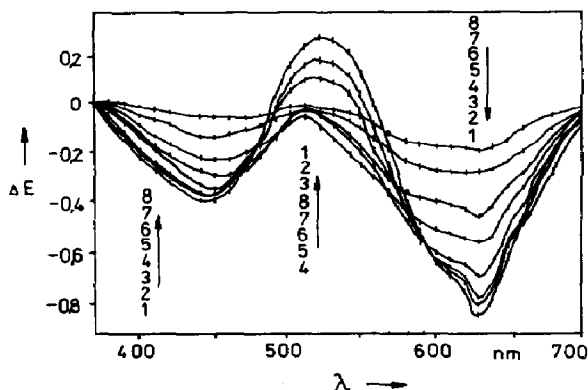
Fig. 5. Difference spectra of a flash-irradiated solution of dithizone in dry acetone at 25 °C obtained after various delay times (initial concentration C_0 = 2.55 × 10^{-6} M; distance d = 10 cm): curve 1, 0.5 ms; curve 2, 1.5 ms; curve 3, 5.0 ms; curve 4, 8.0 ms; curve 5, 25.0 ms; curve 6, 50.0 ms; curve 7, 100 ms; curve 8, 150 ms.

A. The majority of the ED diagrams are non-linear (Fig. 6), whereas linear extinction difference quotient (EDQ) diagrams are obtained (Fig. 7). In contrast with the n-hexane solutions no isosbestic points appear during the relaxation. A completely analogous behaviour was observed in acetonitrile. The kinetics of the relaxation are best described by a doubly exponential rate law. We found relaxation times τ_1 = 3.26 ± 0.03 ms and τ_2 = 110 ± 1 ms for acetone and τ_1 = 1.33 ± 0.3 ms and τ_2 = 11.1 ± 0.2 ms for acetonitrile solutions (mean values from 30 measurements). With acetonitrile solutions containing about 4.5 × 10^{-2} M H_2O or D_2O isotope effects of τ_1^D/τ_1^H = 1.9 and τ_2^D/τ_2^H = 5.8 were obtained. Whereas the first relaxation time is not changed by the presence of water the second relaxation is slowed down by a factor of 3 compared with that of the dry solutions.

It must be concluded from these results that in acetone and acetonitrile a third isomer C of dithizone is formed in a dark reaction from the isomer B.
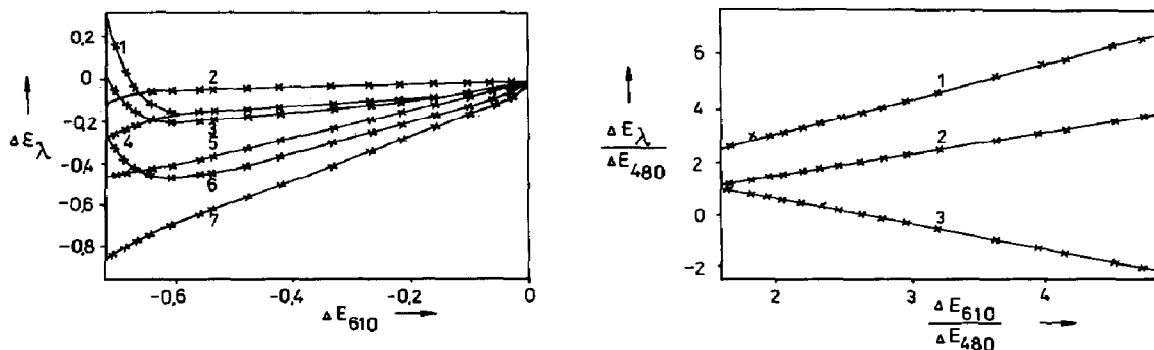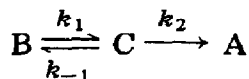

Fig. 6. ED diagrams obtained from the difference spectra shown in Fig. 5: curve 1, λ = 530 nm; curve 2, λ = 370 nm; curve 3, λ = 490 nm; curve 4, λ = 400 nm; curve 5, λ = 450 nm; curve 6, λ = 570 nm; curve 7, λ = 640 nm.
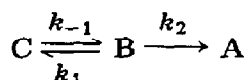
Fig. 7. EDQ diagrams obtained from the difference spectra shown in Fig. 5: curve 1, λ = 610 nm; curve 2, λ = 440 nm; curve 3, λ = 530 nm.

We may conclude from the difference spectra (Fig. 5) that the molar absorptivity of this species is small compared with that of A and B throughout the visible spectral region and its first absorption maximum is located at shorter wavelengths than those of A and B, but we are unable to present an estimate of its spectrum.

The reciprocal relaxation times resulting from both reaction schemes

$$B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \overset{k_2}{\longrightarrow} A$$

and

$$C \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} B \overset{k_2}{\longrightarrow} A$$

are

$$\theta_{1,2} = \frac{1}{2}(k_1 + k_{-1} + k_2) \pm \frac{1}{2}\{(k_1 + k_{-1} + k_2)^2 - 4k_1 k_2\}^{1/2}$$

If k_i denotes the variation in any one of the rate constants involved due to an isotopic effect the isotopic effects on θ_1 and θ_2 can be approximately expressed by

$$\frac{\theta_{1,2}^H}{\theta_{1,2}^D} \approx \left(1 + \frac{\partial \theta_{1,2}}{\partial k_i}\right)^{-1}$$

Because $\partial \theta_1 / \partial k_i > \partial \theta_2 / \partial k_i$ it is obvious that the isotope effect for the faster relaxation should exceed that observed for the slower relaxation. The opposite was experimentally observed which is in favour of the simpler scheme

$$B \overset{k_1}{\longrightarrow} C \overset{k_2}{\longrightarrow} A$$
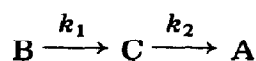
where $\tau_1 = 1/k_1$ and $\tau_2 = 1/k_2$.

4. Conclusions

By keeping in mind the results presented for some metal dithizonates [1 - 8], S-methyl dithizone [10, 11] and some other formazans [22] it also seems possible to interpret the observed photochromism of dithizone in terms of a photoisomerization which involves a geometrical isomerization and a proton transfer reaction. All photochromic metal dithizonates hitherto known can be well described by a simple

$$A \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} B$$
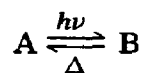
kinetic scheme. For dithizone itself this applies only to the non-polar aprotic solvent hexane whereas in the more polar solvents acetone and acetonitrile

the phenomenological description requires the assumption of an A–C–B system. For the closely related *S*-methyl dithizone we were able to show that even three transients occur in the course of the reversible phototransformations [11, 12].

The lifetime of the metastable photoisomer of dithizone in hexane is smaller by three orders of magnitude than that of mercury(II) dithizonate [5]. Furthermore, dithizone is photoreversible whereas the quantum yield for the reverse photoreaction of mercury(II) dithizonate has been found to be negligibly small [5]. The quantum yields for the forward photoreaction also differ appreciably. The missing oxygen quenching observed for the photoreaction of dithizone may suggest a singlet pathway. However, because only scarce information about the nature of the photoreactive state of the metal dithizonates is available any comparison of the photobehaviour of the metal complexes and the ligand itself seems questionable on the basis of present knowledge.

The kinetic isotope effect $k_H/k_D = 5.5$ observed for the thermal back reaction clearly indicates that a proton transfer reaction acts as a rate-determining step. From the Brønsted coefficient for the base-catalysed reaction it has to be concluded that this proton transfer reaction is endergonic. Thus, an intermediate state is postulated from which a geometrical isomerization starts which shows a lower activation energy than does the proton transfer and which renders the overall relaxation exergonic. This interpretation is consistent with the occurrence of the flat region in the Brønsted plot which is found well below the diffusion-controlled limit. However, as indicated by the appreciable isotope effect also observed in that flat region we believe that this description is still an oversimplification and we are still far from a resolution of the overall relaxation into elementary reactions.

The structure of the green form A of dithizone (Fig. 8) has been well established [13, 15]. On the basis of the surprising correspondence of the visible absorption spectra of the red form B and of the dithizone monoanion, for which a structure has been derived by Pemberton and Buck [23] from Raman spectroscopic measurements, and also with reference to the obvious analogy with other compounds of the formazane series (see refs. 10, 11 and 22) it seems to be reasonable to assume a structure with one six-membered hydrogen-bridged ring for the red form B of dithizone (Fig. 8). The second hydrogen atom on the basis of the present results cannot be localized. Although the conjugation in the ring is less we prefer the thione over the thiol tautomer because of the isotope effect. It is hardly possible to formulate an elementary reaction which directly converts A to B because
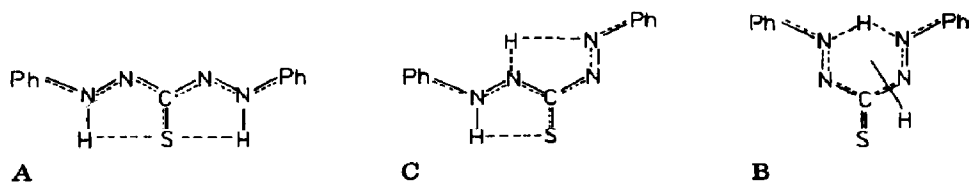

Fig. 8. Structure of dithizone and the proposed structures of its phototransients.

two C—N bonds have to be rotated in addition to a proton transfer. If only one C—N bond is isomerized a structure similar to that of C is obtained. This might be identified with the intermediate state postulated for the relaxation in hexane and which is directly detected in acetone and acetonitrile.

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