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Photochromism of mercury(II) dithizonate in solution

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Abstract

The photochromism of mercury(II) dithizonate was investigated in different organic solvents. The complex is photochromic under steady illumination with visible light. Color change is observed from orange to blue under different interference filters at λ=436, 526, 550 nm. A process of photochemical degradation is obtained in acetonitrile (CH_3CN) and tetrahydrofurane (THF). The photochromic process of mercury(II) dithizonate is discussed in the point of view of the specific influence of the solvents and the presence of their isomeric forms.

Keywords: Photochromism; Mercury dithizonate; Visible light; Interference; Filters

1. Introduction

Metal dithizonates $Me(HDz)_n$ form an interesting class of photochromic complexes. In spite of the fact that several dyes as spiropyrans, fulgides and diarylethenes have dominated in the world of photochromism, the interest in metal dithizonates still exists. The reasons for that are that dithizone forms strongly colored complexes with many different metals; the synthesis of the complexes is a simple chemical process; the photochromic cycle can be repeated many times; the complexes are compatible with different mediums as solvents, polymers, host–guest systems; the complexes can be attached to the polymer chain, glass surfaces, textile, paper; to utilize such rotational movement of photochromic dithizonate complexes for characterizing the polymeric systems — molecular characterization of physical aging; analysis of free volume distribution in polymer films; analysis of segmental and side chain mobility of polymers at molecular level.

Metal dithizonate complexes are one of the earliest organic dyes that were found to exhibit a photochromism. Irradiation by visible light of solutions of mercury(II) bis(dithizonate) ($Hg(HDz)_2$) in organic solvents induces a reversible change of the normal orange-yellow color to an intense royal-blue color [1,2]. These color changes can be repeated many times. After these articles, the photochemistry of $Hg(HDz)_2$ and organomercury-dithizonate complex (R-HgDz) has been extensively investigated [3–5]. The photochromism of many heavy metal dithizonates was observable apart from $Hg(HDz)_2$, the rates of the thermal return reactions were very fast for conventional measurements. On the basis of the spectral and kinetic studies Meriwether et al. proposed the structure of the normal form for the ground state in solution and solid state as shown in Fig. 1 [4].

The photochromic transformation involves a *trans–cis* isomerization about the C=N bond and N-to-N hydrogen transfer of the normal form into the isomer B, which shows lower absorption intensity. The reason for the comparatively long-wavelength absorption of B might be the torsion about the C–N single bond. Form B may revert photochemical as well as thermal to the original form (Fig. 2).

Recent studies using continuous and laser pulse photolysis have elucidated details of the kinetics but the possible transformations of the activated form were not discussed [6]. Although several authors have noted light sensitivity in this class of compounds, no detailed investigations of photochemical effects were done by using an interference filters and the influence of different solvents [1–5].

In connection with our intentions to use photochromic systems for the construction of light-sensitive molecular devices, it was very important to know the behaviour of the normal and activated form of $Hg(HDz)_2$ in polar and non-polar solvents. The effect of the photochromic processes will depend on the other processes in the system as isomerization, presence of short living intermediates,

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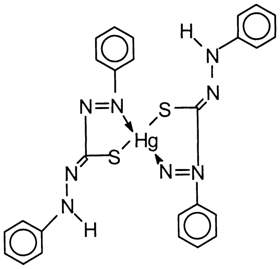


Fig. 1. Structure of the normal form for the ground state in solution and solid state.

mechanism of the reaction, characteristics of the solvents and their participation as subsidiary medium.

This paper evaluates $Hg(HDz)_2$ in terms of color response range on the basis of its photochromic behaviour in different solvents and radiation conditions.

2. Materials and methods

$Hg(HDz)_2$ was synthesized and purified by the procedure described in [3]. Chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), benzene (C_6H_6), CH_3CN and THF were used as solvents. All were of spectral grade and used without further purification. Typical concentrations employed were around 4×10^{-4} mol/l. Absorption spectra were recorded on a Perkin-Elmer 19 UV/VIS spectrophotometer. The energy absorbed by the samples was determined by measuring the light intensity with a power meter in front of the quartz cell. The following interference filters were used for different wavelength regions, i.e. 436, 526, 550 nm, as well as visible light.

The laser experiments were carried out with He–Ne laser (λ=633 nm). The molar extinction coefficients are found by the law of Beer–Lambert ($A=\varepsilon cl$), where A is the optical density, c is the concentration of absorbing form (mol dm^{-3}) and l is the path length (cm).

3. Results and discussion

We directed our attention to two points of view: the photochemical behaviour of $Hg(HDz)_2$ in polar and non-polar solvents and usage of different interference filters [1,2].

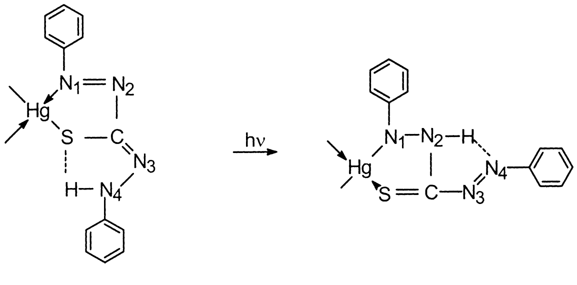


Fig. 2. Reversible process of the photoactivated form.

The absorption spectra of the complex in different solvents are described in Table 1.

In all the solvents used, the complex displays one strong band in the 480–500 nm region (normal form A). The absorption of the activated form was monitored at maximum in the 595–610 nm region. The values of the molar extinction coefficients, ε, of the bands are in accordance with the literature data [3,4].

$Hg(HDz)_2$ was photochromic under our test conditions with visible light in $CHCl_3$, CH_2Cl_2 and C_6H_6. A visual color difference between the samples before and after irradiation was taken as a positive evidence of photochromism. The main photochemical product of the reaction is form B (absorption band in the 590–610 nm region). The complex is activated by visible light above 420 nm in the region containing the first visible absorption band. Before irradiation, $Hg(HDz)_2$ is stable in its normal isomeric form and gives an orange color in $CHCl_3$ (Fig. 3).

The equilibrium between the normal and activated forms is strongly shifted to the normal form.

During irradiation with different filters the position of the absorption maximum in the 550–610 nm region is different (Table 2, Fig. 3). In this region there are three absorption maxima: at 580 nm (filter 436 nm), 590 nm (filter 526 nm) and 603 nm (filter 550 nm) (Fig. 4).

The irradiated time at each wavelength corresponds to that at which the absorption of the excited state reached a constant value. Maximum average value for the absorption of the activated species appears at about 600 nm. Since different interference filters have different thicknesses, the

Table 1
The spectral data of the normal A and activated forms B of $Hg(HDz)_2$ in different solvents and irradiation with visible light[a]

Solvent	Dielectric constant (ε)	$Hg(HDz)_2$			
		Form A		Form B	
		λ_{max} (nm)	ε (dm^{-3} mol^{-1} cm^{-1})	λ_{max} (nm)	ε (dm^{-3} mol^{-1} cm^{-1})
$CHCl_3$	4.7	498	(102564)	598	(86363)
CH_2Cl_2	6.7	498	(71794)	602	(50588)
THF	7.32	498	(94871)	–	
C_6H_6	9.78	498	(66666)	605	(60000)
CH_3CN	36.2	484	(41025)	–	

[a] Concentration: 3.9×10^{-4} mol/l.

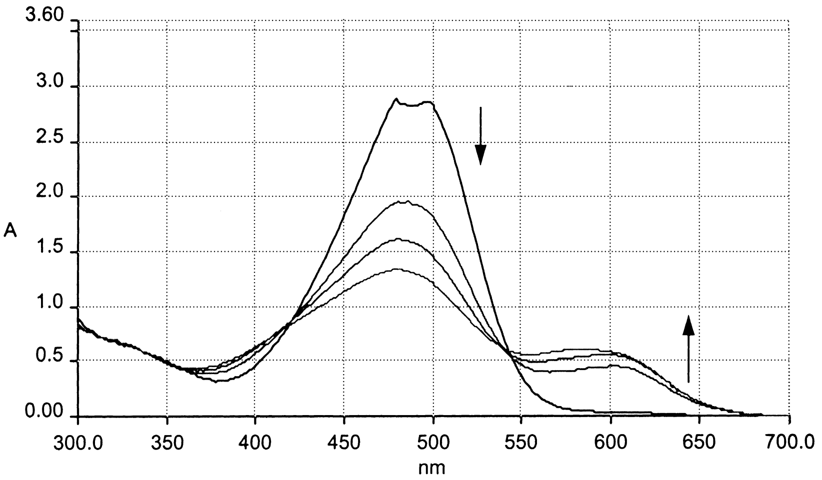
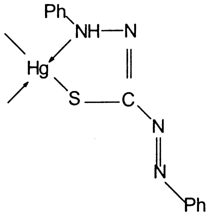


Fig. 3. The spectral changes of $Hg(HDz)_2$ in $CHCl_3$ ($c=3.9\times10^{-4}$ mol/1) due to filter cut-off 550 nm; power 72 mW/cm^2; τ_{irr}: 0, 60, 90, 120 s.

radiant energy transmitted by each is not the same. The same absorption value for the steady state was obtained with different filters of the same nominal wavelength but at different irradiation times.

The experimental results are in accordance with the results of U.-W. Grummt et al. about the photochemistry of dithizone in solution [4]. They explain the observed photochromism in terms of photoisomerization, which involves a geometrical isomerization and a proton transfer reaction. In this direction, are the conclusions about the presence of isomers of the activated form of $Hg(HDz)_2$ of Meriwether [5]. The band at 603 nm is characteristic of the activated form B (Fig. 2). The structure is formed by the cleavage of the hydrogen bond to the sulfur atom, *cis−trans* isomerization around the C=N bond, and the formation of a new hydrogen bridge to N_2. The changes in the structure are drastic and many organic compounds having this structure in a conjugated system are known to be blue [8]. It is very important to note that the activated form B is the main product of the photoreaction. The shoulders in the longer wavelength bands at 580 and 590 nm (Figs. 3 and 4) can be connected with the transformation of the form B in the isomeric form C with N=N–H and S–C=N fragments [5,7].



Form C

The hydrogen bond in fragment N=N–H in ground state will be weak because of the low basicity of the azo nitrogen atom. But in the excited state of the form B the basicity of the nitrogen atom can be changed and such a process will be effective. The possibility for the formation of other isomer, derived by the cleavage of the Hg–N bond is small because of structural problems. This conclusion is in accordance with the data for the number of photosynthesized molecules of the activated form B for 1 min (Table 3).

The photoinduced formation of the molecules of the form B with filters 526 and 550 nm is more effective with 88% and 94%, respectively. But with filter 436 nm the obtained molecules are half, 47%. This difference shows that a part of the form B converts into other species. Since the reversible reaction is completed, the conclusion about the presence of the process of transformation of the form B into other isomeric forms can be made. The isosbestic points in the spectra are a proof for the presence of the photochromic process only with the absence of the degradation. Therefore there is need from enough energy for the transformation of the form B. For 1 min, the total energy transmitted in the system with filter 436 nm is 32.4 J/cm^2. For filter 550 nm the value was 4.32 J/cm^2. When the irradiation time is enough (long period of irradiation), a process of conversion of form B and with filter 550 nm takes place (Fig. 1). It is interesting to note that in PMMA film, doped with $Hg(HDz)_2$ under the influence of UV light, a process of conversion of form A into form B takes place [9]. The polymer matrix restricts strongly the possibilities for the motions of the molecules and the

Table 2
The spectral data of the normal and activated forms of $Hg(HDz)_2$ in $CHCl_3$[a]

Filter, λ (nm)	$Hg(HDz)_2$	
	Form A	Form B
	λ (nm)	λ (nm)
436	498	580
526	498	590
550	498	603

[a] ε_A (dm^{-3} mo1^{-1} cm^{-1})=102564; ε_B (603 nm) (dm^{-3} mo1^{-1}cm^{-1}) =47500; filter cut-off: 436, 526, 550 nm.

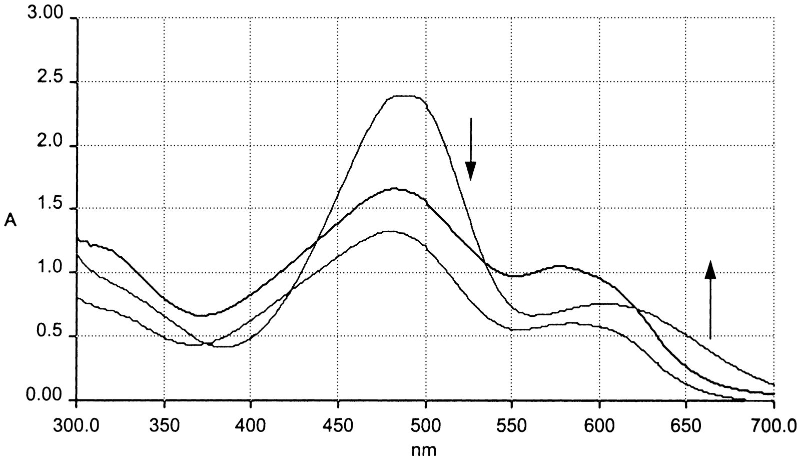


Fig. 4. The spectral changes of $Hg(HDz)_2$ in $CHCl_3$ (c=3.9×10^{-4} mol/l) due to filter cut-off; 436, 526 and 550 nm.

Table 3
The number of the changed molecules of form A and the photosynthesized molecules of the activated form B for 1 min in $CHCl_3$

Filter, λ (nm)	Number of changed molecules of form A	Number of photosynthesized molecules of form B
436	8.6×10^{18}	4.03×10^{18}
526	5.8×10^{18}	5.1×10^{18}
550	6.5×10^{18}	6.2×10^{18}

Table 4
The number of the changed molecules of form A and the photosynthesized molecules of activated form B for 1 min in CH_2Cl_2

Filter, λ (nm)	Number of changed molecules of form A	Number of photosynthesized molecules of form B
436	1.5×10^{19}	1.4×10^{19}
526	–	–
550	1.3×10^{19}	0.3×10^{19}

process of the rotation of the fragments. This fact shows that the conversion of the form B into other isomers can be the influence of the mechanism of the process and the properties of the matrix. The usage of He–Ne laser (632.8 nm, power 2 mW) to a reversible reaction does not give a positive result. We found a process of degradation.

The photochromic behaviour of $Hg(HDz)_2$ in dichloromethane is close to that in $CHCl_3$ (Fig. 5).

Before irradiation the solution has an orange color (496 nm, ε=78974) and after 5 s of exposure to visible light the color changes to blue (602 nm, ε=13461). There is no difference in the position of the absorption maximum around 600 nm. As it can be seen from Table 4, when the irradiation is with filter 436 nm the transformation is 93%.

The comparison with the results of $CHCl_3$ shows two differences. First, with 436 nm the transformation is only to form B. When we used a filter (λ=526 nm) we find a difference in comparison with $CHCl_3$. During irradiation, the maximum at 498 nm decreases and not appears at a maximum of 602 nm. This result indicates that there is no transformation of isomer A to isomer B, only a process of

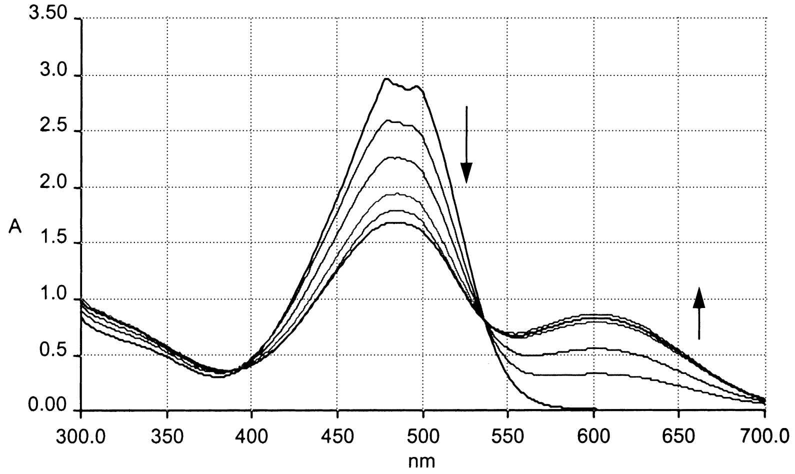


Fig. 5. The spectral changes of $Hg(HDz)_2$ in CH_2Cl_2 (c=3.9×10^{-4} mol/l) due to visible light irradiation (5 s UV irradiation).

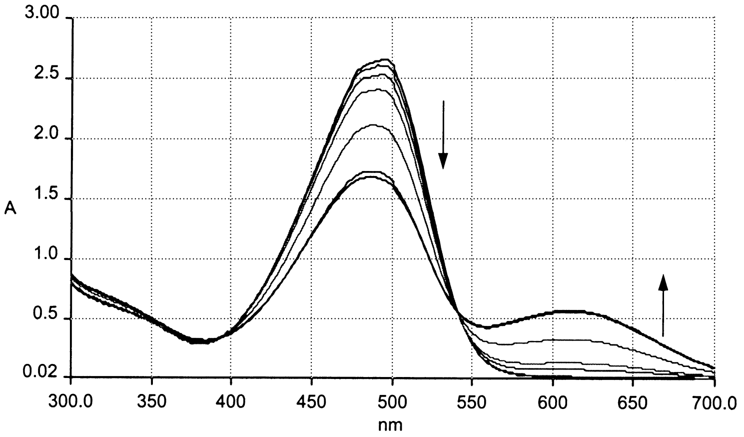


Fig. 6. The spectral changes of $Hg(HDz)_2$ in benzene (c=3.9×10^{-4} mol/l) due to visible light irradiation (5 s UV irradiation).

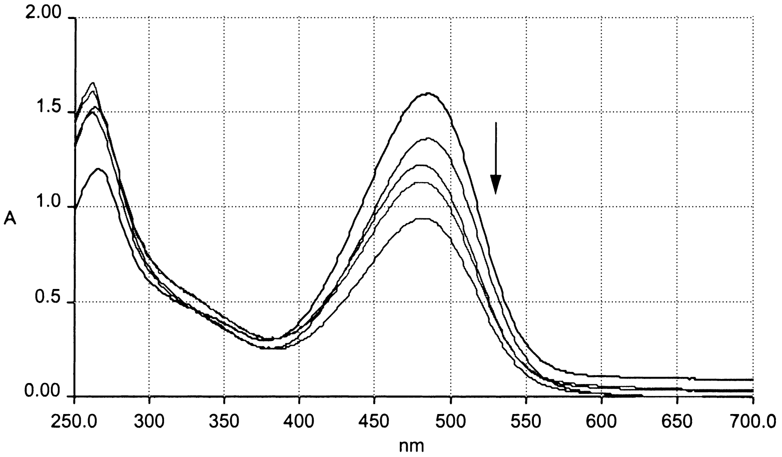


Fig. 7. The spectral changes of $Hg(Hdz)_2$ in CH_3CN (c=3.9×10^{-4} mol/l) due to visible light irradiation.

degradation. The number of the photosynthesized molecules B is around 24%. The results indicate that the main product of the photoreaction is form B. The differences can be written on the influence of the solvent, although the difference in the polarity of the $CHCl_3$ (dielectric constant ε=4.7) and CH_2Cl_2 (ε=6.7) is not so large. The specific influence of the solvent can be connected with the short lifetime of the other isomers. On the other hand, it can be noted that the results are similar as with filter 526 nm, a partial process of degradation. The results in $CHCl_3$ and CH_2Cl_2 indicate that the photoinduced conversion between the different isomeric species of the activated form is very sensitive to the reaction conditions: polarity of the solvents, total energy of the irradiation, the structure of the species [10]. This conclusion is in accordance with the results in benzene (dielectric constant ε=9.78). When solutions of $Hg(HDz)_2$ in benzene were irradiated with visible light they changed their normal orange color to blue. But there is no change in the position of the absorption maximum in the area of the activated form with different filters. The presence of the isosbestic points is a proof for the existence of a process of conversion between form A and form B (Fig. 6).

With He–Ne laser (λ=633 nm, power 2 mW) there is a reversible process. Six reversible cycles are repeated in benzene without a process of degradation. In contrast with $CHCl_3$, CH_2Cl_2 and benzene in CH_3CN (dielectric constant ε=36.2) and THF (dielectric constant ε=7.32) during irradiation there is no maximum at longer wavelengths. There is only decrease of the maximum, which characterized form A. This is a proof for a process of photodegradation (Fig. 7).

The result in acetonitrile and THF can be connected with the specific influence of the solvent. For example, there is a possibility of the acetonitrile molecule to form an exiplex with the excited molecule of the form B (Fig. 8), [11], or to be realized specific interaction with the compound [12].

Then transformation of the complex will be in the other direction of degradation. This result is in strong confirmation

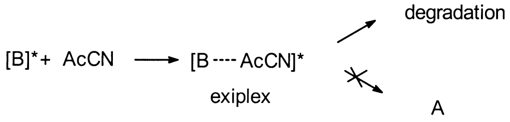


Fig. 8. Formation of complex with acetonitrile molecule.

that the polarity of the solvents is not the only important factor in the process of photochromism of $Hg(HDz)_2$.

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