SOME STUDIES ON THE PHOTOCHROMISM OF MERCURY DITHIZONATE

By

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SOME STUDIES ON THE PHOTOCHROMISM
OF MERCURY DITHIZONATE

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CHAPTER I

INTRODUCTION

Discovery of dithizone dates back to 1878 when Emil Fischer was doing extensive studies on the derivatives of phenylhydrazine (1). Its introduction as an analytical reagent, however, did not occur until 1925 when Hellmuth Fischer reported on the metal complexes of dithizone and its applications in chemical analysis (2). Dithizone forms brilliantly colored complexes with a variety of heavy metal ions, almost insoluble in water and soluble in a variety of organic solvents. It has been used in the detection and determination of trace metals. The reagent has proven to be very valuable and there is a considerable amount of literature on its applications (3).

Many workers have commented on the sensitivity to light of solutions of some of these dithizonates, and have recommended that experiments be carried out in the dark or under diffused light. While studying the determination of traces of mercury, Irving, Andrew and Risdon (4), did not experience any unusual effects until the year's first period of extended sunshine in March of 1946. At this time, a solution of mercury dithizonate in chloroform was observed to change from an orange color to an intense blue color. The orange color returned slowly in the dark. The phenomenon is called photochromism.

The photochromism of metal dithizonates was found to have some adverse effects on the colorimetric analytical applications of these complexes. This led to an extensive study of a number of photochromic metal dithizonates to obtain a better understanding of their photochemical behavior. Attempts have been made to determine the structures of the ground and excited state of some of the dithizonates. Mercury dithizonates have a slower return to ground state and kinetic studies of the relaxation process have been performed (5,6).

The purpose of this work was to determine (1) the energy range of photons responsible for the photochromism of mercury dithizonate, (2) the photochromic relaxation of silver dithizonate and (3) the effect of silver dithizonate on the relaxation of mercury dithizonate. The experimental procedures involved and the results obtained form the subject of this thesis.

CHAPTER II

PHOTOCHROMISM

History of Photochromism

The phenomenon by which a chemical substance changes color when exposed to light and reverts back to its original color in the dark was originally called phototropy. Marckwald (7), in 1899, observed that benzo-1-naphthyridine and tetrachloro-1,2-ketonaphthalenone underwent a reversible photoreaction or phototropy. He concluded that this was a purely physical phenomenon.

Biologists have been using the term phototropy to describe the alignment of certain plants towards light. To avoid confusion the term photochromism has been adopted to describe the physico-chemical change. Photochromism literally means coloration by light.

The first mention of photochromism in the literature was made by ter Meer (8). He reported that the potassium salt of dinitromethane changed color when exposed to exciting radiation. Another early report was made by Phipson (9), who observed a gate that looked black by day and white by night. It is now presumed that the paint was similar in composition to the pigment lithopone.

Serious research in this field began in the early

1900's. It was concentrated on the synthesis of the materials and the kind of exciting radiation required. The mechanisms of the photochromic processes and accompanying energy relationships were not of much concern. This situation did not change until a few decades later. During the 1930's a few systems were studied and the mechanism involved in the process were discussed. Photochromism of semicarbazones was found to be an effect of mesomerism. The change is brought about by the displacement of the electrons which resulted in the formation of a polar structure (10). It was suggested that the photochromism of malachite green leuco cyanide in aqueous ethanol solution is the result of ionization followed by hydrolysis (11). Renewed interest in photochromism began in the 1940's. A whole new range of compounds, both organic and inorganic were studied. More extensive studies were conducted on rates and mechanisms. Attempts were made to determine the ground and excited state of the molecules involved (5,6).

Definitions

Photochromism was, at first, associated with a reversible photochemical change caused by the irradiation of light resulting in a color change. This is no longer acceptable because researchers have proved that the phenomenon extends beyond the visible region. Brown (12), defined photochromism as a "reversible change of a single chemical species between two states having distinguishably different absorption spectra, such a change being induced in at least one direction by the action of electromagnetic radiation ". It can be represented by the equation.

$$A(\lambda 1) \xrightleftharpoons{h\nu} B(\lambda 2) \qquad (1)$$

The radiation and the spectral changes usually occur in the ultraviolet, visible or infrared regions. The change in the reverse direction occurs spontaneously and is thermally induced.

The chemical species A must be a molecule or an ion. The product B may consist of more than one species that recombine to produce A. The possibility of an intermediate also exists. Normally, the excited state B is thermodynamically less stable. In most cases it is also found to have a more intense color. However, 15,16-dihydropyrene decolorizes on irradiation and spontaneously regenerates its color (1).

Photochromisms in which more than one chemical species are involved are also known to occur. A more general definition would, therefore, include such processes. Adamson (13), while defining photochromism as a reversible light induced color change gave the following equation to illustrate the process.

$$A\ (+\text{ other reactants}) \xrightleftharpoons[\phi_B \,,\, k_B]{\phi_A \,,\, k_A} B(+\text{ other products}) \qquad (2)$$

where ϕ denotes the quantum yield of the reaction and k denotes the rate coefficient.

In Adamson's definition of photochromism the reaction is a simple one that does not form any intermediates. The system can be classified as either singly or doubly photochromic. In a singly photochromic system the reaction is induced by electromagnetic radiation in one direction and the relaxation is a spontaneous thermal process. An example of this type is the photoinduced tautomerization of 2-hydroxy, 5-methyl, azobenzene to its hydrazone.

In a doubly photochromic system the forward and reverse reactions are photochemical in nature. For example, when a solution of the stilbene, [2.2] meta cyclophane-1-ene was irradiated with ultraviolet light in the absence of oxygen it gave the product 4,5,15,16 tetrahydropyrene, which absorbs at 500 nm. The tautomeric return to stilbene is affected by illumination with visible light. The energy difference between the two forms corresponds to that of visible light.

Mechanisms of Photochromic Processes

Photochromism occurs in a large number of compounds both organic and inorganic. Anils, disufoxides, hydrazones, semicarbazones, stilbene derivatives and spiro compounds are among the typical classes of organic compounds that undergo photochromism. Typical inorganic compounds include metal oxides, alkaline earth metal sulfides, titanates, some mercury and copper compounds, and some transition metal carbonyls. It is also found in glasses and some living systems.

The photochromic processes can be classified on the basis of their mechanisms. The mechanisms involved are (1) heterolytic cleavage, (2) homolytic cleavage, (3) cis-trans isomerism, (4) tautomerism, and (5) development of centers of color in inorganic solids.

Heterolytic cleavage

Heterolytic cleavage is one of the processes which has been extensively studied. When irradiated with light, the energy absorbed by the activated molecule causes the cleavage of a single bond. It results in the formation of a charged species. These species may be stable and unreactive due to their structure. Usually, they recombine to regenerate the original species. The three main classes that undergo photochromism by this kind of cleavage are spiropyrans, triaryl methanes, and polymethines.

Fischer and Hirshberg (14) first observed the photocoloration of spiropyrans. They exhibit photochromism in a wide range of solvents.The cleavage of the 1,2 single bond is believed to be responsible for the photochromism of the spiropyrans.

Triaryl methane dyes are decolorized when treated with various anions (e.g. cyanide or hydroxyl). The derivatives are called leuco dye cyanide and hydroxide. Colorless solutions of these leuco dye derivatives become colored on exposure to ultraviolet light which is the color of the starting dye and this fades on standing. The leuco dye cyanide of trichloro crystal violet is photochromic. Polymethine dyes when bleached and then irradiated with light of 300-400 nm were found to be photochromic.

Numerous derivatives of 2,3-epoxycyclopentadiene have been reported to undergo a photoinduced color change (15). The heterolytic cleavage of the three membered ring gives rise to a dipolar intermediate, which is the cause of the photochromism in this class of compounds.

Homolytic Cleavage

This results in the formation of free radicals. Pyrroles, hydrazines, disulfides and nitroso dimers are some of the classes that undergo photochromism via homolytic cleavage. The rates of return from the colored form are very fast and have very few practical applications.Some examples of this category are discussed.

When bis-tetra phenyl pyrrole is oxidized in a benzene solution of lead oxide, a radical is produced in equilibrium with a dimer (16). The photochromism of the solution can be explained by the dissociation of the dimer to give a redish-purple solution of the radical.

Colorless solutions of dimeric 3-methyl-3-nitroso butane-2-one in ethanol, chloroform or benzene on irradiation with light from a mercury lamp produces a monomeric species that absorbs in the red (17).

Photochromic color changes among aryl disulfides were first observed by Smiles (18). He found that at least one aryl group must contain an amino group in the para position for color change to occur.

Cis-Trans Isomerism

It is the trans isomer that is usually more thermodynamically stable and the cis isomer is thermally converted back to the trans form. So the general isomerization process can be symbolized by

$$\mathrm{Trans} \underset{h\nu' \text{ or-heat}}{\overset{h\nu'}{\rightleftharpoons}} \mathrm{Cis} \tag{3}$$

The cis isomer usually absorbs at shorter wavelengths than the trans.

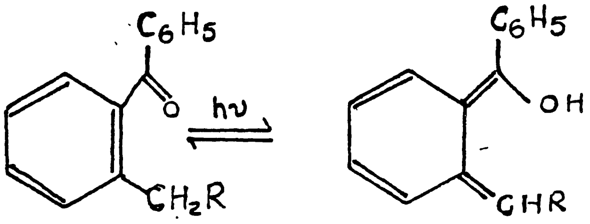
The compounds that undergo photochromism through this mechanism fall into two main categories.

Compounds that isomerize about a C=C bond. The indigoid dyes fall under this intersting category(19). The R can be any alkyl or acyl group but not a H atom. Replacement by a sulfur atom also causes photochromism.

Compounds that isomerize about a N=N bond. Azobenzene and substituted derivatives have a principle band in the uv region, and a weak absorption at 450 nm. When irradiated they are converted to the cis form and the absorbance increases. In this case there is a deepening of color due to trans-cis isomerization (20). Cis-trans isomerization also occurs around a C=N bond. The photochromism of the metal dithizonates belongs to this classification and will be discussed in more detail in Chapter III. Cis-trans isomerization about multiple unsaturated linkages is responsible for the photochromism in some compounds (24).

Tautomerism

When a photochemical shift in the equilibrium between isomers occur, changing their relative concentrations, it is referred to as photochromic tautomerism. Two types of photochromic tautomerism exists. One is by hydrogen transfer. Reversible photo-enolization of o-alkyl benzophenone follows this mechanism (21).



(4)

In cases of phototropic tautomerism, the hydrogen transfer occurs via a six membered transition state. The thermally stable forms are the ortho substituted aromatics. Hydrogen transfer produces quinoid structures.

Valence tautomerism occurs with a change in the position of the valence bonds. Bonds are broken with new positions of attachment but the groups involved remain connected by a chain of atoms. Some compounds discussed, under other specific classifications may also come under this category.

One of the oldest classes of compounds found to be photochromic are the fulgides. Their mechanisms, however, have been elucidated in the more recent years (22). They are derivatives of dimethylene succinic anhydrides. Diphenyl fulgides undergo a valence tautomerism on irradiation to give dihydronaphthalene derivatives.

Inorganic Photochromism

Inorganic solids that exhibit photochromic phenomena have a large band gap (3-12 ev). They have very small absorption in the visible region. When irradiated with photons of energies corresponding to the band gaps, metastable centers are formed. These absorb light in the visible region and give rise to characteristic color. They can return to ground state by heating or excitation within the band gap. The photochromic phenomena is attributed to (1) formation of electron-hole pair by the excitation of the inorganic solid, (2) color centers formed by the trapping of free carriers and (3) bleaching of color centers by various recombination processes.

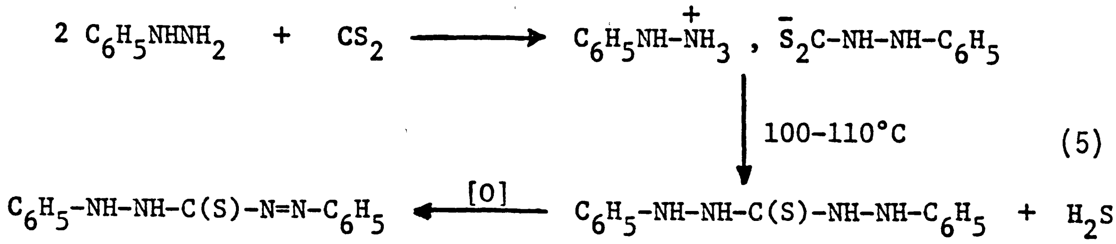
Color centers can be produced in alkali halides, alkaline earth halides, and alkali metal azides, and hence can all be called photochromic. A large number of metal oxides also undergo photochromism by eletron trapping in defects within a crystal (23).

CHAPTER III

PHOTOCHROMISM OF DITHIZONE AND METAL DITHIZONATES

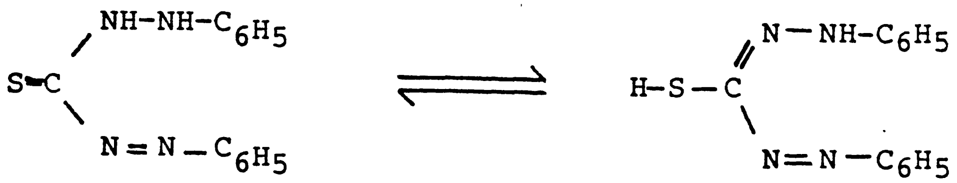
Dithizone

When solutions of carbon disulfide and phenylhydrazine in organic solvents were mixed an unstable white salt was obtained(1). On heating, loss of hydrogen sulfide occured and it resulted in the formation of diphenylsulfocarbazide. When warmed with dilute alkali in the presence of oxygen it undergoes oxidation to give diphenylthiocarbazone, better known as dithizone. The reaction occurs as shown.



$$\begin{tikzcd}
2\,C_6H_5NHNH_2 + CS_2 \arrow[r] & C_6H_5NH\text{-}\overset{+}{N}H_3\ ,\ \overset{-}{S}_2C\text{-}NH\text{-}NH\text{-}C_6H_5 \arrow[d, "100\text{-}110°C"] \\
C_6H_5\text{-}NH\text{-}NH\text{-}C(S)\text{-}N{=}N\text{-}C_6H_5 & C_6H_5\text{-}NH\text{-}NH\text{-}C(S)\text{-}NH\text{-}NH\text{-}C_6H_5 + H_2S \arrow[l, "{[O]}"']
\end{tikzcd} \tag{5}$$

Dithizone (H_2Dz) forms a violet-black crystalline powder. It has the chemical formula $C_{13}H_{12}N_4S$ and a molecular weight of 256.32 g/mole. It is insoluble in water. It is however, soluble in a variety of organic solvents. The solubility is low in alicyclic and aliphatic hydrocarbons, alcohols and ketones. The solubility is higher in aromatic hydrocarbons. The highest solubility is achieved in chlorinated hydrocarbon solvents. Dithizone dissolves in basic aqueous solutions to give an orange color. This is due to the formation of the primary dithizonate anion, HDz^-. The absorption spectrum of dithizone in an organic solvent shows two peaks (Figure 1). The relative heights vary from one solvent to another. The two peaks are believed to correspond to two forms of dithizone in equilibrium in solution. The two tautomeric forms are that of the thione and thiol forms.

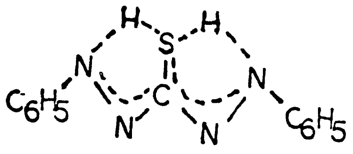


Thione Thiol

(6)

The absorption maxima in chloroform are at 442 and 605 nm, while in carbon tetrachloride they are at 450 and 620 nm respectively. The peak at longer wavelength corresponds to the thione form.

The structure of the solid dithizone was determined by X-ray crystallography (23). It was found from measured bond lengths that the electrons in the chain are delocalized, and form a five membered ring with the sulfur and hydrogen atoms. The following structure was proposed for crystalline dithizone.



(7)

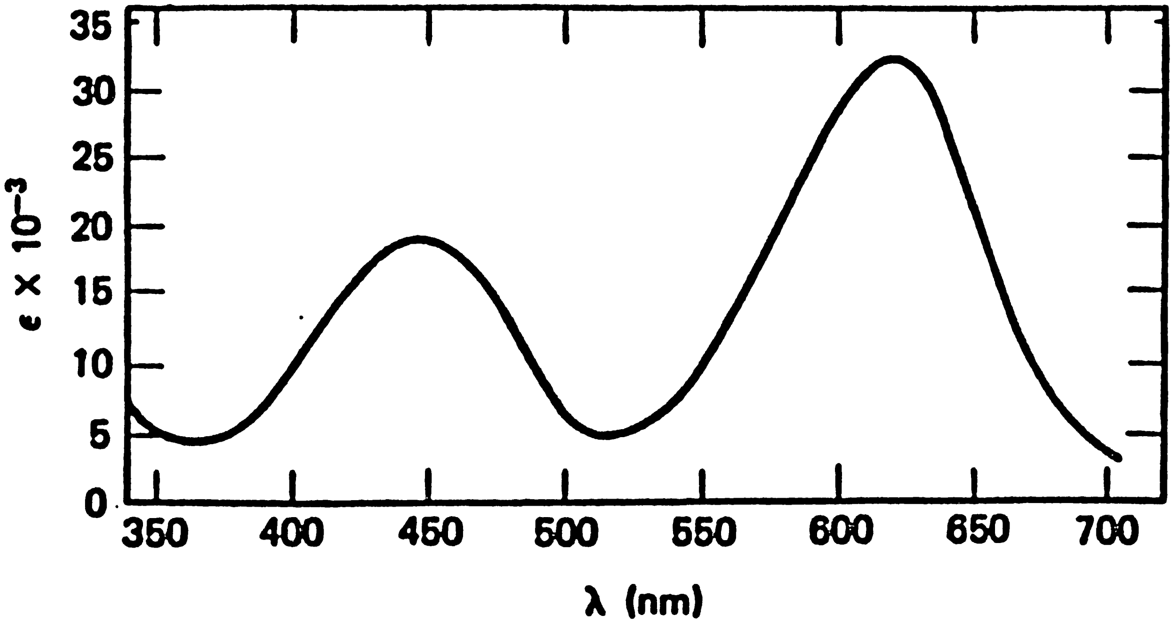
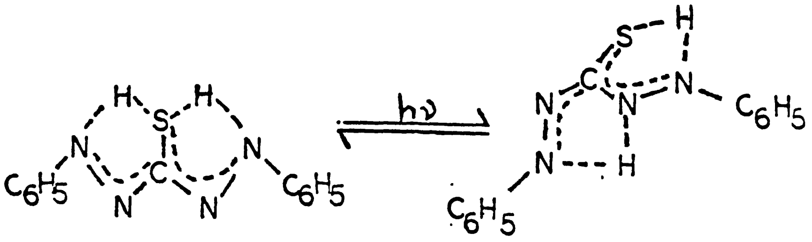


Figure 1. Absorption Spectrum of Dithizone in CCl_4

Meriwether (5) reported that dithizone is itself photochromic. They did not offer any experimental evidence to substantiate the claim. The electronic spectra and the photochromism of dithizone were studied by Coleman et.al (31). They found that, when a solution of dithizone, in a dry nonpolar solvent, was irradiated with full intensity of a near infrared Cary 14 W lamp a red metastable form was produced. This metastable form returned rapidly to the original green color. Dithizone showed a bleaching of color, resulting in the decrease of λmax values at 605nm and 409nm when irradiated with unfiltered light from a General Electric Quartzline Lamp(24).

Photochromism of Sulfur alkylated dithizones occur via the trans-cis isomerization (25). The same mechanism has been proposed for the dithizone. Goodwin and Mottola (24), proposed a structure for the excited state of dithizone and gave the equation to describe the photochromism of dithizone. The excited form results from a rearrangement of a bond from an N-H-S to a N-H-N bond.



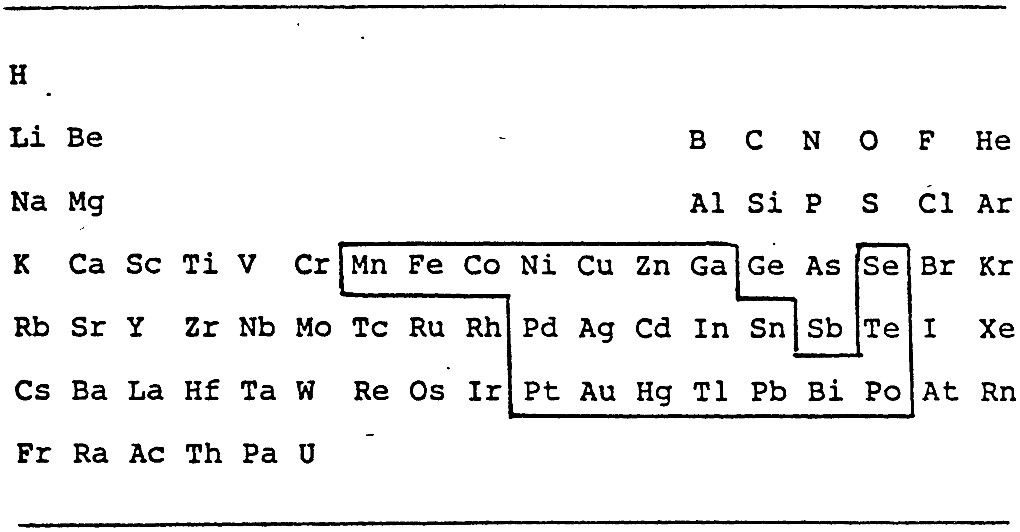
(8)

Metal dithizonates

Dithizone contains two active hydrogen atoms. Each of the hydrogens can be replaced by an equivalent of metal. All

TABLE I

METALS WHICH FORM DITHIZONATES



H																	
Li	Be											B	C	N	O	F	He
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Th	Pa	U												

the metals that form dithizonates are shown in Table I.

When one of the hydrogens is replaced by a metal a primary dithizonate is formed. The metal can be extracted from an aqueous solution of the cation with dithizone into an organic phase containing an excess of the dithizone ligand. These are complexes of the mono anion. The equation that describes it is as follows.

$$M^{+n} + nH_2Dz \longrightarrow M(HDz)_n + nH^+ \qquad (9)$$

This assumed that the reaction of the reagent occurs in the thione form of dithizone. S-Alkylated derivatives of dithizone do not form similar chelates. This supports the presence of metal-sulfur bonds in dithizonates (25). The existence of the metal-sufur bond is further substantiated by X-ray study on the crystals of mercury dithizonate. The structure was first reported by Harding (26), who showed that mercury is tetrahedrally coordinated to the sulfur and nitrogen atoms of the dithizone molecule. Primary copper(II) dithizonate was found to be similar to the mercury complex except that it had a square planar configuration about the central metal atom (27). X-Ray structure determinaton of zinc dithizonate has shown that the molecule has two bidentate dithizone molecules coordinated tetrahedrally through two sulfur and nitrogen atoms. Other dithizonates with similar structures are $Ni(HDz)_2$, $Pd(HDz)_2$ and $Pt(HDz)_2$ (28).

Fewer metals form secondary dithizonates than primary dithizonates. Due to the stoichiometry of the dithizonates formed, dithizone has been thought to behave as a diprotic acid. The infrared spectrum shows the absence of a N-H bond. The 1:1 complex was assumed to be formed from the enol form of dithizone (2). In the case of Cu(II) chelate, however, it has been proven that it is not a keto-enol equilibrium but a Cu(I)-Cu(II) redox equilibrium that is responsible for the formation of the secondary dithizonate. The unusual coordination number of copper to form the 1:1 complex can be achieved through intermolecular bonding(30).

Spectral studies

The solution spectra of metal dithizonates show the presence of intense visible absorption bands. All complexes display one strong band in the 450-550 nm region and one or two other bands at longer wavelengths. These strong bands show high molar absorptivities ($\varepsilon \approx 10^5$) (TableII). They are to a large extent independent of the metal. Since dithizone itself has bands of similar intensity it has been suggested that these transitions are primarily associated with the delocalized electronic system of the ligand.

Dithizonates can be divided into four groups on the basis of their infrared spectra of the solids (5).

1. $Mn(HDz)_2.H_2O$, $Zn(HDz)_2$, $Cd(HDz)_2$,
$Hg(HDz)_2$, $Pb(HDz)_2$, $Sn_2(HDz)_2.2H_2O$,
$Bi(HDz)_3$.
2. $Ag(HDz)H_2$, $Au(HDz)(OH)_2$, $Tl(HDz)$ and
$Cu(HDz)_2$.

TABLE II

λ MAX AND ε MAX OF SOME DITHIZONATES IN CCL_4 AND $CHCL_3$

Dithizonate	λmax nm		εmax (lit/mol.cm)x10^{-4}	
	CCl_4	$CHCl_3$	CCl_4	$CHCl_3$
Ag,P	460		2.91	
Ag,S		470		3.1
Cu(I),P	480	490	2.13	2.8
Cu(II),P	550	545	4.52	
Cu(II),S	450	445	2.27	
Hg(I),P		490		3.06
Hg(II),P	490		7.2	
Hg(II),S	515		2.36	

P-Primary S-Secondary

3. $Ni(HDz)_2$, $Pd(HDz)_2$, $PdDz.2H_2O$, $Pt(HDz)_2$.
4. $Os(HDz)_3$ and $Co(HDz)_2$.

$CuDz.2H_2O$ and Ag_2Dz have IR spectra unlike other dithizonates.

Solubility

Solubility of metal dithizonates in usual organic solvents are limited (5). At room temperature, saturated solutions in benzene are in the range of 10^{-4}-10^{-5}M. The highest solubility is found in chloroform. Spectrophotometric studies can be conducted in solvents like CCl_4, CH_2Cl_2, and THF. Secondary dithizonates are less soluble than primary dithizonates.

Dithizonates are insoluble in water and only slightly soluble in ethanol. Alcohol solutions have a different color from non polar organic solvents. Dimethylformamide, pyridine and acetonitrile solutions also have unusual colors, suggesting an interaction with the solvent.

Solution properties of complexes are also affected by the pH, which suggest pH dependent structural changes. A brown chloroform solution of $Cu(HDz)_2$ turned violet when shaken with aqueous acid and returned to its original color when shaken with aqueous base.

Photochromism of metal dithizonates

The photochromic property of mercury dithizonate was recognized in the 1940's (4). The first extensive work was conducted by Meriwether et.al (5). They prepared a large number of metal dithizonates. The 24 dithizonates prepared were characterized and their photochemical behavior was studied in solid and in solution. Tungsten and low pressure mercury sources were used for irradiation. None of the secondary dithizonates were observed to be photochromic.

Only mercury dithizonate was found to be photochromic in the solid state. When mercury dithizonate crystals were smeared on a porous plate and irradiated with visible light the color changed from orange to brown and then violet. The return to orange was very slow.

Nine of the complexes were found to be photochromic in solution. Photochromic dithizonates, conditions in which the phenomenon is observed and the rate of return to ground state are listed in Table III. The color change observed in these complexes is from orange or red to blue or violet. Exceptions to this are palladium and platinum complexes which have color changes from green to yellow.This gives an indication that the ligand is of primary importance in the photochromic process (5).

The spectrum of the excited state could be obtained only in a few cases because of the fast return to ground state. These return rates range from a half life of 30 secs for mercury at 25^{O}C to 1 sec for cadmium at -80^{O}C.

The metal, however, has a definite influence on the rate of return to ground state. There is no significant pattern in the order of metals with increasing return rates.

TABLE III

PHOTOCHROMIC REACTIONS OF PRIMARY METAL DITHIZONATES

Dithizonate	Solvent	Colour, and absorption maximum (nm)		Temp./°C	Approx. return time/s
		Normal form	Activated form		
$Ag(HDz),H_2O$	Tetrahydrofuran	Yellow (470)	Violet	25	2—5
				10	40—60
$Zn(HDz)_2$	Tetrahydrofuran, ethyl acetate	Red	Violet-blue	−40	<1
	Methylene chloride	Red (530)	Violet-blue	25	1—2
$Cd(HDz)_2$	Tetrahydrofuran, acetone	Orange (500)	Violet	−80	<1
$Hg(HDz)_2$	Benzene, chloroform, methylene chloride	Orange (490)	Blue (605)	25	30—90
$Pb(HDz)_2$	Tetrahydrofuran	Red (520)	Blue	−80	<1
$BiCl(HDz)_2$	Tetrahydrofuran, methylene chloride	Orange (490)	Blue (605)	−40	2—5
$Pd(HDz)_2$ 'green'	Methylene chloride	Green	Orange	−10	1—2
	Benzene	Green	Orange	25	5—10
	Chloroform	Green (450, 640)	Blue (450, 520, 570, 630)	25	5—10
$Pt(HDz)_2$	Benzene, carbon tetrachloride	Yellow (490, 708)	Red	25	1—2
$Bi(HDz)_3$	Methylene chloride, xylene	Orange (498)	Violet	−30	<1

The effect of the metal can be explained on the basis of (1) the metal-ligand bond strength, (2) differences in stereochemistry of the complexes, (3) effect of solvent and (4) different reaction mechanisms(6).

When measured by the rate of return to ground state,the photochromic property is subjected to the polarity of solvents and the presence of acids and bases. The stongest photochromic effects are observed in dry non polar solvents like benzene, toluene, chloroform, and carbon tetrachloride. The presence of hydroxylic solvent and organic acids and bases results in an accelaration of return to ground state.

The photochemical stability of metal dithizonates have been studied (5). It was found that the metal complex had a stabilizing effect on the light tolerance of the ligand. This can be attributed to the harmless dissipation of energy during the photochromic process.

Kinetics of photochromism

Photochromic systems have unique characteristics and it is of interest to determine the structure of the excited form of the complex and to determine the mechanism involved. To achieve these goals various researchers have followed the kinetics of the reaction and infrared spectral changes during irradiation (6,33,24). Due to slower return rates, photochromism of mercury dithizonate has recieved the greatest attention. Some kinetic studies have been performed on silver dithizonates.

Meriwether et al (6) followed the return reaction of mercury dithizonate spectrophotometrically, monitoring the disappearance of the absorption of the excited species at 605 nm and the reappearance of the ground state at 490 nm. Pseudo first-order rate coefficients were calculated from both the measurements and they agreed with each other within experimental error. This proved that there was no intermediate species present. The rate coefficient was found to be a function of (1) the concentration of of the complex, (2) water content and (3) time elapsed since the preparartion of solution. Some of rate coefficients reported for mercury and silver dithizonates by Meriwether are tabulated in Table IV.

Geosling et al (33) found that there was no large effect of water or complex concentration on the rate coefficients. The rate constant for mercury dithizonate were distinctly lower than that reported by Meriwether et.al. The rate coefficients obtained for the silver dithizonate were, however, comparable with those obtained by Meriwether. They also reported an uncertainty in the reproducibility of the data, from run to run. Cleaning and conditioning of glassware were found to greatly affect the reproducibility of rate studies. It was suspected that the return to ground state may be affected by dust and other surface catalysis.

Goodwin and Mottola (24), found that the reproducibility of data was obtained when clean glassware was soaked in a solution of dithizone for a period of time

TABLE IV

RATE COEFFICIENTS FOR THE RETURN REACTION OF MERCURY DITHIZONATE AND SILVER DITTHIZONATE

Complex	Temperature °C	Rate Coeff. sec^{-1}	Ref.
$Hg(HDz)_2$	25	$2.7x10^{-3}$	6
Ag(HDz)	11.5	$1.1x10^{-2}$	6
$Hg(HDz)_2$	24	$0.5x10^{-3}$	33
Ag(HDz)	11.5	$1.7x10^{-2}$	33
$Hg(HDz)_2$	25	$2.6x10^{-3}$	24

before use. Solutions of mercury dithizonate were allowed to stand for 4 to 20 hrs in the dark before making any measurements. They confirmed that the return rate coefficient was independent of the complex concentration. While studying the photochromic behavior under solvent extraction some observations were made, which pointed out the fact that, the presence of excess free ligand, plays an important role in the rate of return to ground state. The rates of return were found to be dependent on the ligand to metal ratio (Figure 2).

The photochromic excitation of mercury dithizonate did not involve an intermediate. This is substantiated by the single isobestic point that lies between the two bands, for the ground and excited state (5).

On the basis of the X-ray crystallographic study of Harding (26) and the infrared spectra, Meriwether assigned the structure of solid mercury dithizonate to the complex in solution, in the ground state (6). Since there was no long lived intermediate it was assumed that the excited state must be an isomer of the ground state. A dissociation-recombination process was ruled out due to the absence of free dithizone or anions in the spectrum of the excited state. It was assumed that an intramolecular hydrogen transfer occured with water acting as a proton transfer agent. This theory was strengthened by the dependence of the rate constants on water content. His mechanism involved a single ligand-metal chelate ring

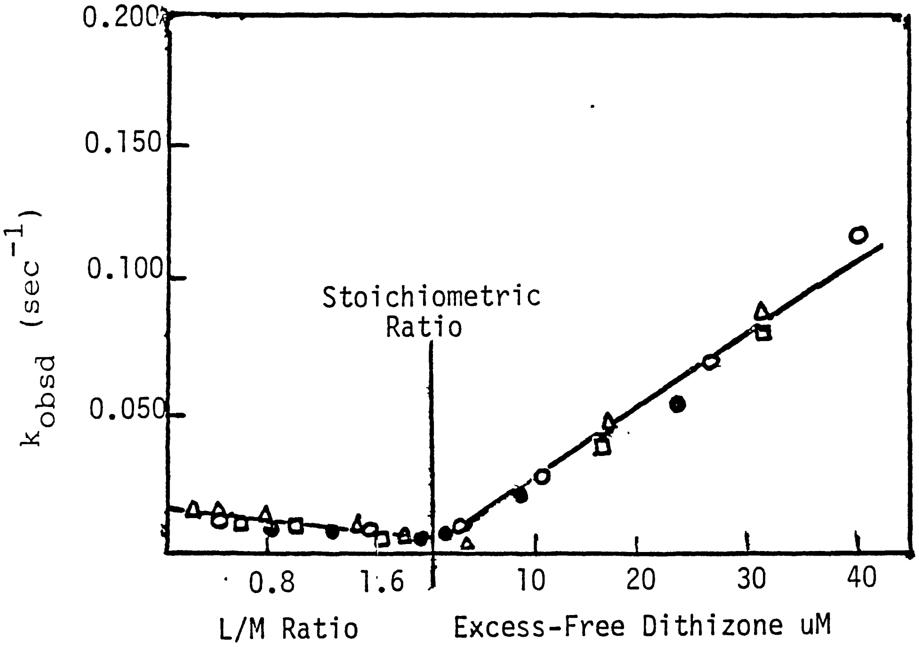


Figure 2. Effect of Ligand to Metal Ratio on the Rate Coefficient of Mercury Dithizonate Relaxation. Temp. 25°C; $Hg(HDz)_2$: (○) 10 uM, (□) 15uM, (△) 20 uM; (●) 30 uM.

system.

Geosling (33) found that the configuration of ground and excited state were the same for all dithizonates and concluded that the ligand isomerizes simultaneously.

Photochromic process was proposed by Goodwin and Mottola (24) (Figure 3).

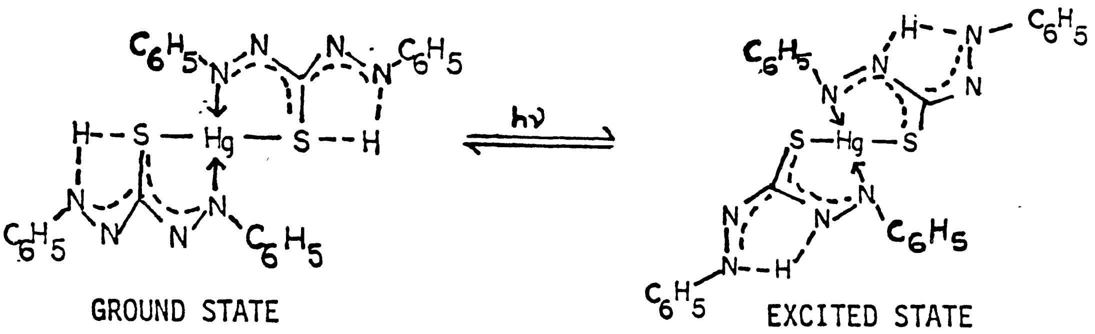


Figure 3. Ground and Excited State of Mercury Dithizonate

It involves a trans-cis isomerization about the C-N bond. The structure of the excited state is indeed an isomer of the Meriwether structure. It does not involve a proton transfer mechanism. It was also seen that the mechanism of photochromism of the metal dithizonate involves the same mechanism as dithizone itself.

CHAPTER IV

EXPERIMENTAL METHODS

Apparatus

The experimental set up used for the study of photochromism was assembled as shown in Figure 4. It consists of the following components.

Source lamp

A 6V tungsten lamp (Chicago Miniature Lamp works No. 1493) was used. It was operated by a MP-1026 regulated power supply (Pacific Precision Instruments, Concord, CA).

Monochromator

A H-10 Jobin-Yvon concave holographic grating monochromator was used.

Cell holder

The cell holder was made to hold a 1cm glass cell. The sample was continuouslly stirred with a magnetic stirrer. The dc motor used (0.25-0.35v, minimum current for operation 25 mA: Edmund Scientific, Barrington, NJ) was operated by a 6V rechargeable battery "Energel" (Radio Shack, Fort Worth, TX). The temperature of the cell was maintained by circulating water through a water jacket using a Lauda/Brinkmann Model K2/R circulator (Brinkmann Instrument Inc.,Westbury, NY).

Detector

The detector used was a HUV-4000B pin photodiode-operational amplifier combination (EG&G Electrooptics, Salem, MA) operated by a 915 Model dual power supply, ±15V, 25 mA (Analog Devices, Norwood, MA).

Irradiation Source

Coastar B-271, 8V, 50w projection lamp (Coastar Inc. , Mt.Vernon, NY) was used for irradiating the sample. The light from the lamp was passed through a heat absorbing glass to filter infrared radiation.

Filters

Interference filters (ALPKEM Corporation, Clackamas, OR) were used to isolate narrow bands of light. Wave lengths of filters used for most of the work were 480, 500, 520, 540 and 560 nm.

Shutters

Shutters were used to control the irradiation and protect the detector from the intense light. These shutters were operated by electrical solenoids (Guardian Electric, Guardian 11-INT-120A, Chicago, IL) actuated by a relay actuator (59306 A, Hewlett-Packard, Palo Alto, CA).

Data Collection and Display

The read out unit consists of a Nicolet 2090 A Explorer digital oscilloscope with a 94 A plug -in and Model-D amplifier (Nicolet Instrument Corp., Madison, WI). The osilloscope and the relay actuator are interfaced with a HP 9825 A desk-top computer through a HP 9878A I/O expander. Other Hewlett-Packard peripherals include 9885M flexible disk drive, 9871A printer and 9862A plotter.

Reagents and solutions

All reagents used were of AR grade. The water used was deionized followed by distillation in a borosilicate glass still equipped with a quartz immersion heater (Corning Model AG-1a, Corning, NY). Benzene used as solvent was of AR grade (Fischer Scientific, Fairlawns, NJ).

Dithizone

Commercially available dithizone (White label Eastman Kodak, Rochester, NY) was found to have low purity, due to the presence of oxidation products and traces of heavy metals (34). Hence it had to be purified before use. The purification process is discussed later in this section.

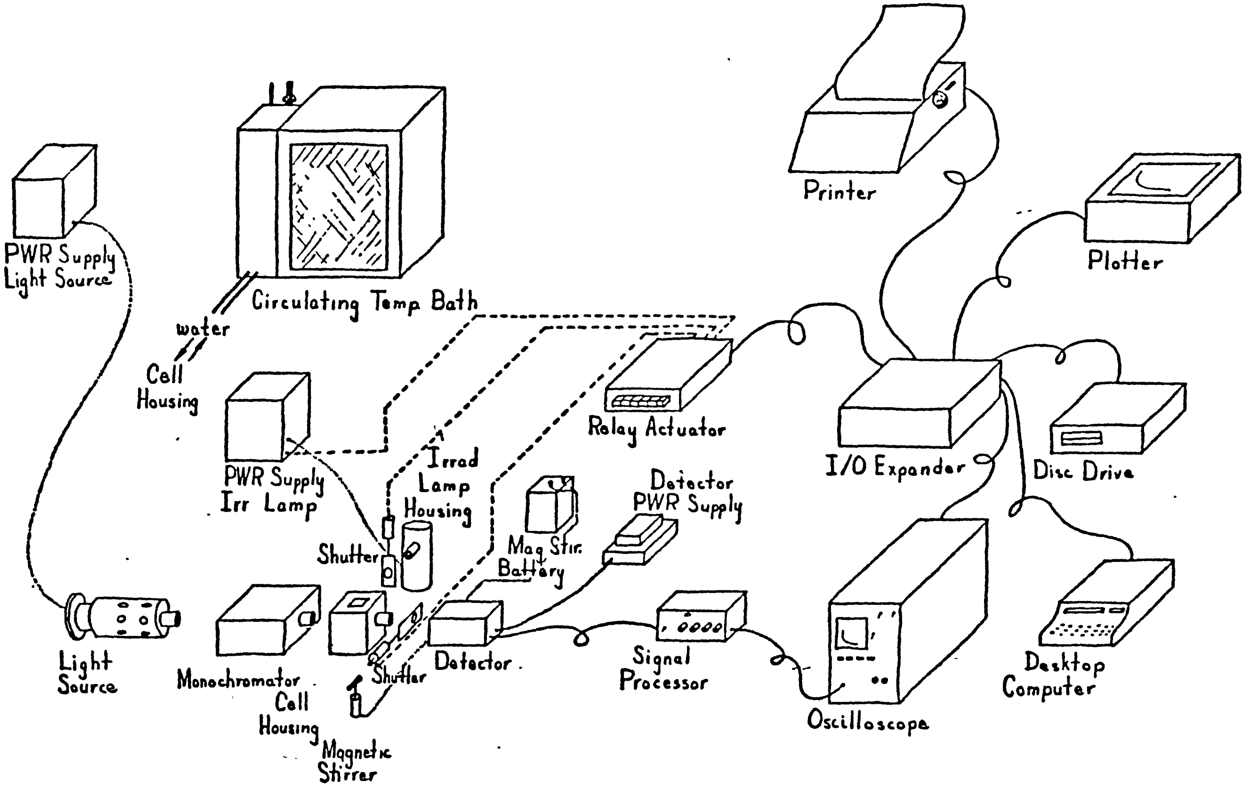


Figure 4. Experimental Setup for the Study of Photochromism

Mercury Dithizonate

The solutions of mercury dithizonate were prepared by dissolving the commercially available solid (Eastman Kodak) in benzene. When these solutions were used as such in experiments there was a lack of reproducibility of results. Photometric titration of the complex with dithizone indicated the presence of uncomplexed mercury in the solutions. A correction had to be made to obtain stoichiometric ligand to metal concentrations, which was important for this study. This was accomplished by photometrically determinig the amount of uncomplexed mercury and adding the required amount of free dithizone to complex with it. Solutions containing excess free ligand were prepared by adding a known amount of free dithizone to a solution containing mercury dithizonate. For experiments involving excess metal in solution two pathways were taken. The first one was the extraction of mercury from aqueous solution of mercuric perchlorate. Equal volumes of excess mercury perchlorate in 0.010 M perchloric acid and dithizone in benzene were shaken in a separatory funnel. Equlilbrium was achieved after 1 min. The extract was filtered through a hydrophobic MN617 WA filter paper (Macherey-Nagel Co., Duren, Germany) and collected in amber bottles and allowed to stand overnight. The amount of dithizone complexed was determined photometrically and the concentration of the complex was obtained. The second pathway involved a similar extraction process. Mercury was extracted from an aqueous solution of mercuric chloride. The dithizonate extract was filtered through a hydrophobic fiter paper and stored as before.

Silver Dithizonate

Silver dithizonate solutions for all experiments were prepared by an extraction procedure. An aqueous solution of silver nitrate in 0.010M nitric acid was used. Equal volumes of the silver solution and dithizone solution were equilibrated. The green color of the dithizone solution changed into a bright orange immediately. The extract was filtered through a hydrophobic filter paper and stored. Solutions of silver dithizonate with excess metal and excess dithizone were prepared following the same procedure used for mercury dithizonate.

Purification of Dithizone

As mentioned earlier the dithizone reagent that was commercially available had a low purity and purification was needed. The following procedure was adopted for the purification of dithizone(34). A saturated solution of dithizone in CCl_4 was prepared and fitered. It was then extracted with 0.080M Ammonia solution. After extracting the aqueous layer from several portions of CCl_4 and rejecting them, the aqueous solution was acidified with sulfuric acid. The pure dithizone was then extracted into pure CCl_4 and dried under vaccum.

Conditioning of Glassware

Contamination of solutions posed a serious problem in the study of photochromism and hence the conditioning of glassware was of utmost importance. Previous researchers had repoted its importance (24,33) and it was found to be highly critical for this study. All glassware was soaked in 3.0M HCl, rinsed with distilled water, dried, filled with a solution of dithizone and allowed to stand. It was then washed, dried and ready for use.

Experimental Procedures

Mercury Dithizonate

Experiments were set up to study the dependence of the photochromic excitation of mercury dithizonate on the energy of irradiation. The experimental set up described in Figure 4 was used. A solution containing a stoichiometric amount of mercury dithizonate was placed in a cell, continuosly stirred and allowed to reach the constant temperature of the circulating water(25°C). The sample was then irradiated with light passing through a filter to provide light of a given energy range. The sample was irradiated for 30 sec and the photochromic relaxation of mercury dithizonate from the excited (blue) to the ground state (orange), was monitored. The absorbance maximum of the excited state was determined. The irradiation times were increased to 60, 120, 180, 240, and 300 sec until a steady state was reached. Thereafter, maximum absorbance did not increase with an increase in irradiation time. The same procedure was repeated for various filters between the wavelengths 400 to 600 nm.

The experiments were repeated with solutions of mercury dithizonate containing excess of free dithizone and excess of mercury.

Silver Dithizonate

The experimental apparatus discussed for mercury dithizonate was also used for the study of the photochromism of silver dithizonate. The effect of irradiation time on silver dithizonate was first determined. The steady state was achieved within 180 sec irradiation. The sample was allowed to reach constant temperature of 20.0°C and then irradiated with light. The photochromic relaxation of the excited species was followed and the absorption maximum determined. Solutions of silver dithizonate with different metal to ligand concentrations were prepared and their photochromic relaxations were followed.

A mixture of silver and mercury dithizonates were prepared. The concentration of mercury was kept constant and the silver concentration was progressively increased. The samples were irradiated with light and the relaxation followed.

Band width of the Interference Filters

The absorption of the interference filters used in the experiment were determined using the Perkin-Elmer 3840 Lamda Array Spectrophotometer. The band width of the filters were measured as shown in Figure 5 and are tabulated in Table V.

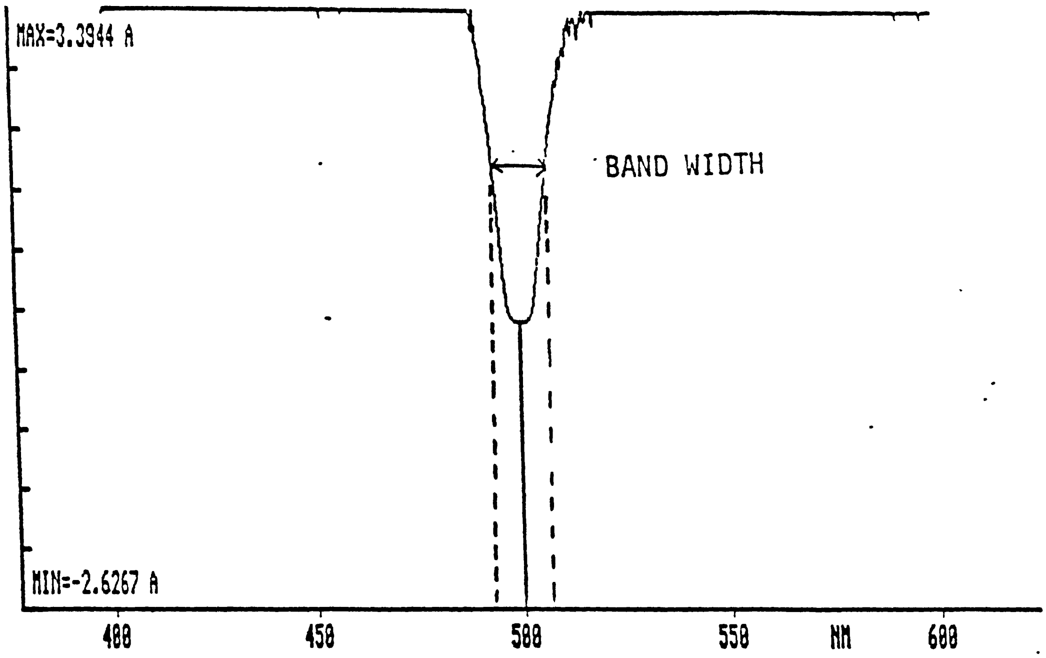


Figure 5. Measurement of Band Width of the Filter used.

TABLE V

BAND WIDTH OF FILTERS USED

Nominal Wavelength nm	Bandwidth nm
480	14.5
500	11.0
520	12.1
540	12.5
560	14.0

CHAPTER V

RESULTS AND DISCUSSION

Determination of the Energy Range of Photons Responsible for the Photochromism of Mercury Dithizonate

Effect of Stoichiometric L/M Ratio

Photochromic relaxation of mercury dithizonate at a stoichiometric ligand to metal ratio was monitored at 25°C, using a wide range of filters. The concentration of the complex was 20 µM and was irradiated for 60 sec. The wavelength of the filters used ranged from 400 to 600 nm. It is seen that the maximum absorbance of the excited species, Amax, increases as the wavelength of irradiation increases until Amax reaches a maximum at 520 nm and then decreases.

When a different set of interference filters were used there was no reproducibility of this trend. There was a direct correlation between the radiant energy and the amount of excitation. The first impression then was that the intensity of transmitted light varied with filters. It was observed that Amax depended on the time of irradiation. So two filters of the same range of wavelength were used to study the photochromism of mercury dithizonate at different irradiation times. It was found that they reached the same steady state Amax.

The experiments were repeated with each filter, increasing the irradiation time until a steady state was reached. It is seen in Figure 6 that the trend noticed earlier was repeated and the use of 520 nm filter gave the maximum absorbance.

Structures of the ground and excited state of mercury dithizonates have been proposed (24) and have been discussed in Chapter III. It was suggested that cis-trans isomerism occurs between the ground and excited state of mercury dithizonate. Hydrogen bonding occurs in the excited state. So the photochromic process involves breaking of a S-H bond to go to the excited state and the breaking of the hydrogen bond with nitrogen during the relaxation process.

Effect on Solutions Containing Excess Dithizone

A solution of mercury dithizonate (20µM) containing an excess of free dithizone (7µM) was irradiated with light from the different filters. With each filter, a steady state was reached when the population of the excited state did not change with an increase in irradiation. The rate of relaxation of mercury dithizonate in the presence of excess free dithizone was reported to be faster (24) and was reflected in this study. Filters of five different nominal wavelengths were used. The excited state increased with increase in wavelength and then decreased. The maximum excitation was observed at 520 nm. The peak obtained was broader, indicating that a broader range of effective wavelengths were involved. It has been known that the ligand dithizone itself undergoes photochromism by the same mechanism as the complex. There is a hydrogen bonding between the ground and excited states of the free ligand and the dithizonate.

Effect on Solutions Containing Excess of Metal

Extraction From Mercury Perchlorate. When an aqueous solution of mercuric perchlorate was extracted with 20 µM dithizone solution, the extractant was found to contain a small excess of mercury(II) in solution. This was irradiated with light of different ranges of wavelengths. The maximum absorption of the excited state was obtained. Figure 6 shows the plot of wavelength vs Amax. It was found to follow the same pattern as the stoichiometric ratio of metal and ligand. The presence of excess mercury in solution does not effect the photochromism of the mercury dithizonate. Some of the anions in solution form mixed ligand complexes of mercury with dithizone. It is seen that in the case of perchlorate, however, this does not occur, which is due to poor complex forming ability of the anion.

Extraction With Mercuric Chloride. Mercury dithizonate extracted from mercuric chloride presented a slightly different picture. Mercury forms mixed ligand complexes with dithizone and chloride, Hg(HDz)Cl (36). This complex is also reported to be photochromic. So when this

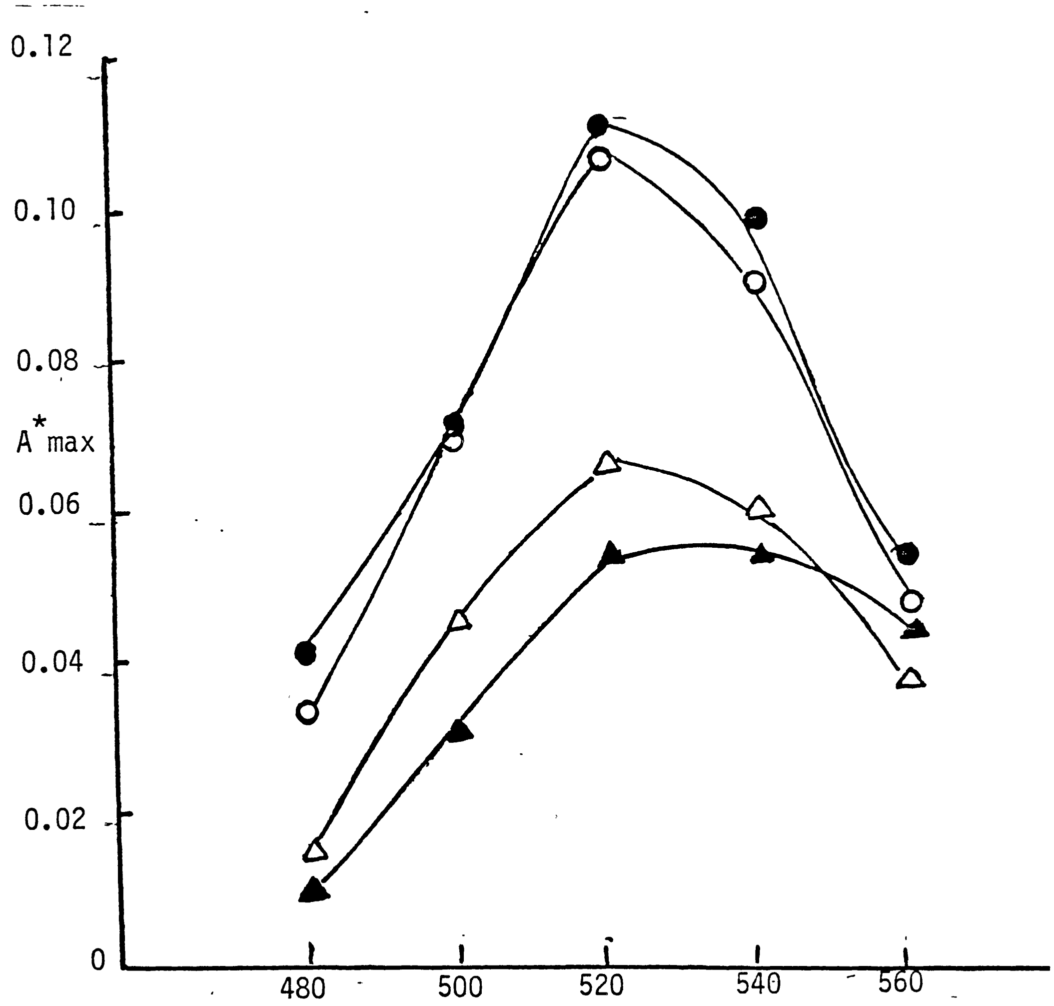


Figure 6. Effect of Wavelegth of Irradiation on the Absorbance of the Excited State of Mercury Dithizonate (●) Stoichiometric L/M ratio, (○) Extraction from perchlorate, (▲) Extraction from Chloride, (△) Excess-Free Dithizone

solution was irradiated with light of different energies the trend observed was somewhat different. The lower wavelengths did not cause significant excitation but higher wavelengths caused significant amounts of the excited species Figure 6.

Some Studies on the Photochromism of Silver Dithizonate

Effect of Irradiation Time on the Population of the Excited State

A solution of silver dithizonate (75 μM) was irradiated for different periods of time. It has been established that the excited state of silver dithizonate absorbs at the same wavelength as the excited state of mercury dithizonate. Hence, the photochromic relaxation of silver dithizonate was monitored at 605 nm. The photosteady state was reached after 180 sec of irradiation under the experimental conditions described. An attempt was made to obtain the energy of maximum efficiency. However, the filters used did not allow to have enough radiant power to cause the photochromic excitation. The experiments were conducted using unfiltered light. The solutions were irradiated for 180 sec and their return to ground state was observed.

Effect of L/M on the Population of Excited State

The amount of silver dithizonate excited under photosteady conditions depends on the amount of excess free ligand present. Stoichiometrically, silver dithizonate forms a 1:1 complex. It was observed that the maximum absorption occurs when this stoichiometric ratio is reached.

Effect of L/M on the Rate Coefficient

The observed rate coefficient, k_{obsd}, for the relaxation of silver dithizonate also depends on the presence of free ligand. It is seen that k_{obsd} increases markedly with increase in the free ligand present in the solution. When an excess of metal is present, i.e. when there is a deficiency of ligand there was little or no effect on the k_{obsd}. This can be seen in Figure 7. The observed effect of L/M on the rate coefficient is similar to the trend that was reported for mercury dithizonate (24).

It is seen that the lowest value of the rate coefficient is observed for a stoichiometric ligand to metal ratio. It is also seen that the concentration of metal chelate itself does not have an effect on the rate coefficient. It can be said that in the absence of excess dithizone the silver dithizonate relaxes to the ground state following first order kinetics. The situation in the presence of free ligand is different. It has already been discussed in Chapter III that the ligand dithizone itself is photochromic. Therefore, when irradiated with light the ligand goes to the excited state and then relaxes back to the ground state. The ligand present in the ground state, however, can facilitate the return of the metal chelate to

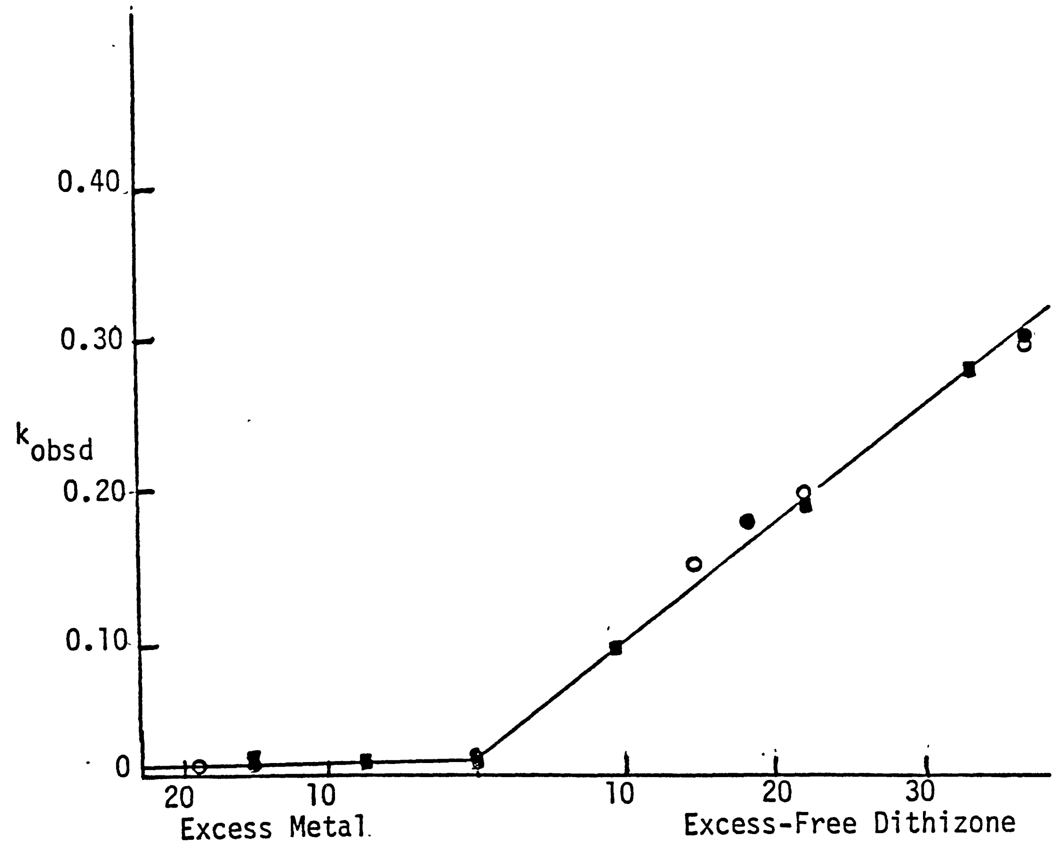


Figure 7. Effect of Ligand to Metal Ratio on the Rate Coefficient of Relaxation of Silver Dithizonate. Ag(HDz) : (■) 75μM, (●) 100 μM, (○) 150 μM.Temp.20° C

the ground state. This can be explained on the basis hydrogen bonding taking place during the photochromic excitation.

Studies of Mercury Dithizonate Relaxation in the Presence of Silver Dithizonate

The concentration of mercury dithizonate was kept constant (10 μM) throughout the experiment. The silver dithizonate ranged from 10 μM to 100 μM. Silver concentrations were therefore in excess (up to 10:1). The mixture was photochemically excited and the relaxation was monitored.

The excited state of both silver and mercury dithizonate absorb at 605 nm. The rates of relaxation are known to be different (6,33). The silver dithizonate relaxes about three times faster than mercury dithizonate. If the two react independently this would indicate that when the photochromic relaxation of a mixture of silver and mercury dithizonate were studied, the first-order plots would have two different slopes, the first corresponding to the faster relaxation of silver dithizonate and the second due to the slower relaxation of mercury dithizonate. This was not found to be the case. A straight line was obtained when $-\ln(A_{\infty}-A_t)$ was plotted versus relaxation time with a single slope (Figure 8). The first order plots for the different concentrations of silver were made. When these staight lines were extrapolated beyond the zero relaxation time they all converged at a point. This would seem to suggest that the photochromic excitation and relaxation followed is that of a single chemical species. The absorbance of the excited state at this extrapolated time was calculated from the corresponding value of $-\ln(A_{\infty}-A_t)$ and it was found to be 0.295. The mercury dithizonate solution (10 μM) has an absorbance of 0.279 when all the complex is in the excited state. The Amax of the excited state of a 100 μM solution of silver dithizonate is 0.058. It would, therfore, be reasonable to assume that what is observed is the effect of silver dithizonate on the photochromic excitation of mercury dithizonate.

The presence of silver dithizonate has a pronounced effect on the rate of relaxation of mercury. The rates of return are accelarated. The new rate coefficient, however, was not found to be an additive function of the mole fractions and the rate coefficients of silver and mercury dithizonate (Figure 9). This was calculated using the equation

$$k'' = k_{Hg}\, f_{Hg} + k_{Ag}\, f_{Ag} \tag{10}$$

The calculated data did not fit the experimental results. There is an increase in the rates with an increase in silver concentration. This is similar to the effect observed when free excess dithizone was present in a solution of mercury dithizonate.

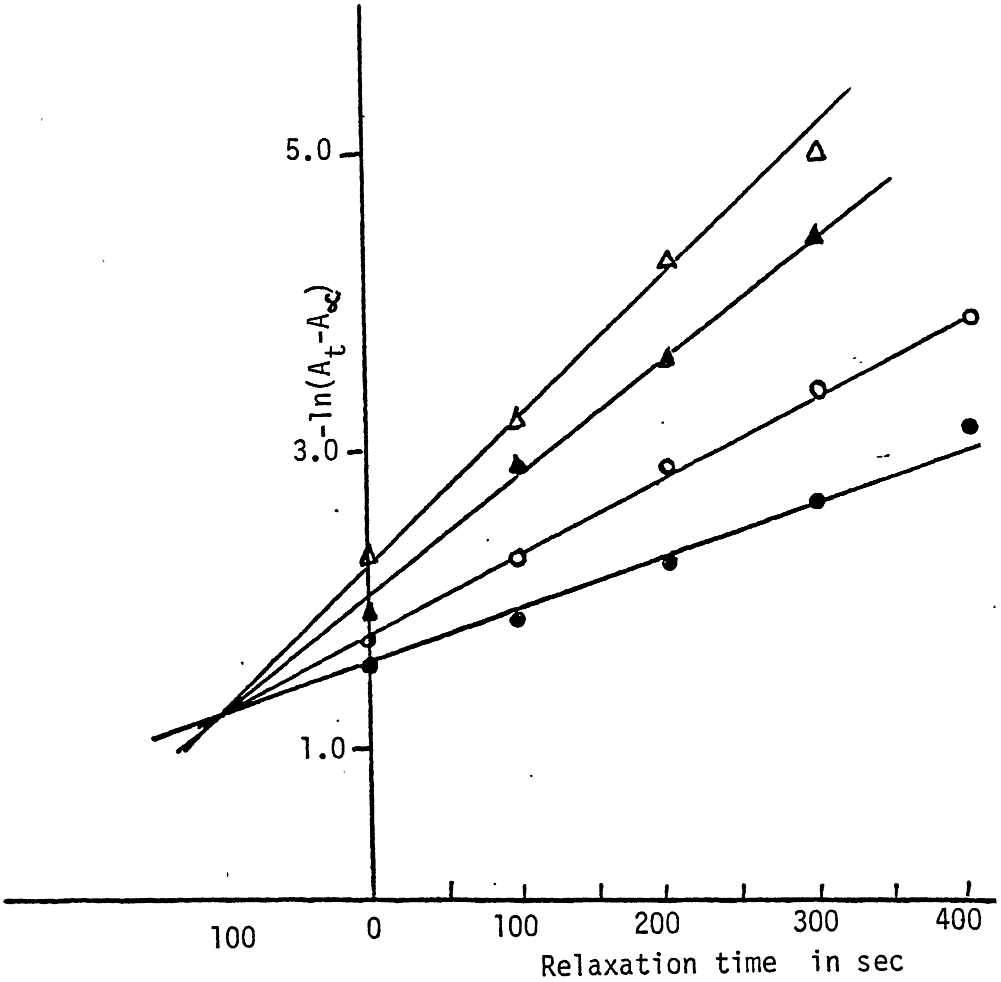


Figure 8. First-order plots of Relaxation of Mercury Mercury Dithizonate in the Presence of Silver Dithizonate [Hg(HDz)$_2$]: 10 μM [Ag(HDz)]: (●) 20μM, (○) 40 μM, (▲) 60 μM, (△) 100 μM.

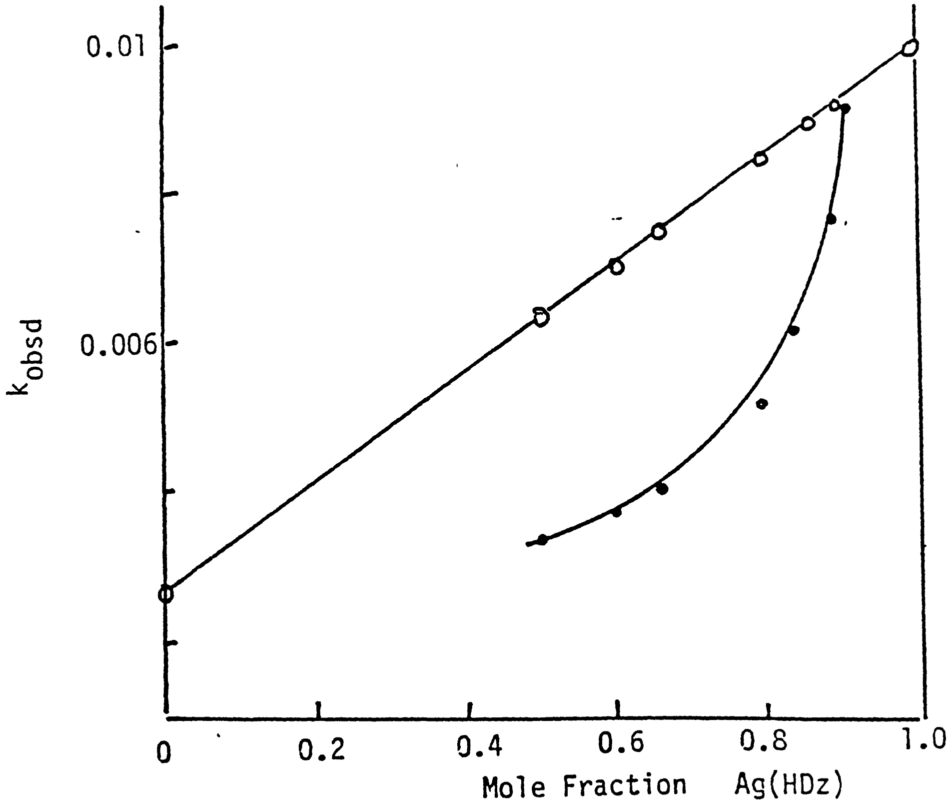


Figure 9. Change in k_{obsd} for the Relaxation of Mercury Dithizonate with the Mole Fraction of Silver Dithizonate present. (○) Calculated (●) Experimental

An equation was developed to show the dependence of the rate coefficient on the silver concentration.

$$k^{*} = k_{Hg} + k\ [Ag(HDz)] \qquad (11)$$

where the k^{*} is observed rate coefficent for the mixture. k_{Hg} is the reported value for the rate coefficient of mercury dithizonate. The value of k is obtained from the known values of k^{*}, k_{Hg} and [Ag(HDz)]. It was found to be a constant 63.2±3.7sec^{-1} M^{-1}. A mechanism for the photochromic relaxation of mercury dithizonate in the presence of silver dithizonate is proposed and shown in Table VI.

The equation for the absorbance is given by

$$A_t = A_{\infty} + A_0\ \{-t(2.7\ x10^{-3})+(63.2x[Ag(HDz)])\} \qquad (12)$$

and fitted with the data. A_t is the absorbance at relaxation time t. A is the absorbance at infinity and A_0 is the absorbance of the excited form that is detected first in zero time. Figure 10 shows the calculated rate profile and the data points from the experimental run and it is found to show good agreement. This would indicate at least the validity of the mathematical model to predict experimental trends. It also gives support to the suggested mechanism. This study indicates that the silver dithizonate present together with mercury dithizonate has an effect

TABLE VI

EFFECT OF SILVER DITHIZONATE ON THE PHOTOCHROMIC RELAXATION OF MERCURY DITHIZONATE

$$\mathrm{Hg(HDz)_2} \underset{k'_{\mathrm{obsd}}}{\overset{h\nu,\ \mathrm{AgHDz}}{\rightleftharpoons}} \mathrm{Hg(HDz)_2}^{*}$$

$$d[\mathrm{Hg(HDz)_2}]/dt = k^{*}\,[\mathrm{Hg(HDz)_2}]^{*}$$

$$k^{*}\,\mathrm{obsd} = (2.7 \pm 0.4) \times 10^{-3} + (63.2 \pm 3.7)\,\mathrm{s^{-1}M^{-1}}\,[\mathrm{Ag(HDz)}]$$

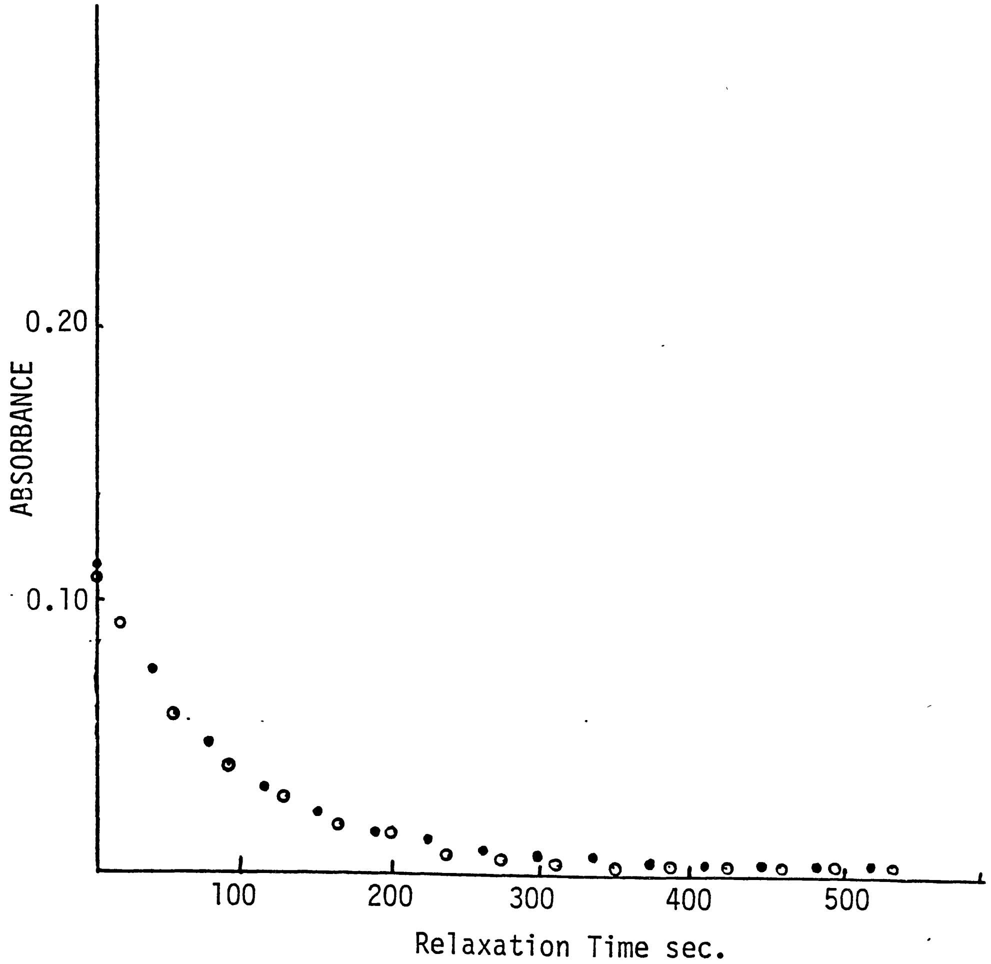


Figure 10. Relaxation Rate Profile of Mercury Dithizonate in the presence of Silver Dithizonate. Fitted data (●); Experimental data(○). [Hg(HDz)$_2$] 10 µM; [Ag(HDz)] 100 µM.

similar to the presence of excess free dithizone in a solution of mercury dithizonate (24) and silver dithizonate, as discussed earlier in the chapter.

It can also be inferred from these results that this photochromic process will be difficult to implement as an analytical tool for the simultaneous determinations of silver and mercury.

CHAPTER VI

CONCLUSION

This work was undertaken to study some of the photochromic properties of metal dithizonates. The two metal complexes considered were mercury and silver dithizonates. The discussion has therefore been divided into two sections.

Earlier work on the photochromism of mercury dithizonates revealed some interesting features (24). The new interest was to determine the energy of the photons more efficient for the excitation of the complex. It was observed that using a 520 nm filter (12.1 nm bandwidth) gave maximum excitation for mercury dithizonate. This was found to be true when free ligand, dithizone, was present in excess. Solutions containing excess of metal were prepared by extraction from an aqueous solution of the chloride and perchlorates. The perchlorate anion did not have any significant effect on the photochromic process. Chloride on the other hand forms mixed-ligand complexes with the mercury which are known to be photochromic. The energy range of photons efficient for the excitation was found to greater.

The concentration of the excited state of silver dithizonate produced on irradiation with light was found to be much less than that for mercury. The rate of relaxation of silver is also much faster. An attempt was made to study the energy of maximum excitation for the silver dithizonate but due to the combined factors of relatively lower radiant power and faster relaxations, the present experimental set up could not be used for such a purpose. The photochromic excitation of silver dithizonate was therefore done with unfiltered light.

Photochromic excitation of silver dithizonate was studied and was found to be independent of the concentratiion of the metal complex. It was found to be dependent on the excess amount of free dithizone present. The photochromic relaxation of dithizone accelerated the rate of return of the excited silver dithizonate to ground state as it does with mercury dithizonate(24).

The study of the effect of silver on mercury dithizonate produced some interesting results. It was found that the photochromic processes of the two complexes were not independent. Silver dithizonate caused an acceleration of the rate of relaxation of mercury dithizonate which was dependent on the concentration of silver. A relationship between the rate coefficients and the concentration of silver dithizonate was developed which was found to provide good agreement with experimental results.

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