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Studies on Photochromism of Primary Silver Dithizonate Complex

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The effect of monochromatic illumination for primary silver dithizonate complex on the photo-induced current was studied. The study showed that a violet colouration of the complex was developed out, and returned again in dark to its original orange-red colouration after a time depending on complex temperature. The creation of partially or completely positive charge on one of the nitrogen atoms due to formation of covalent bonding between it and silver ion instead of coordination one, upon illumination, leads to great increase in the induced photocurrent values. The results showed that the nonirradiated complex has a tetrahedral configuration, whereas the irradiated one has a distorted square pyramidal structure and has also a bivalent silver ion.

INTRODUCTION

Many workers have commented on the sensitivity of solutions of some metal dithizonates in organic solvents to the effects of light, and they have recommended that experiments should be carried out in the dark or in diffused light and that solutions should not be exposed to bright lights during spectrophotometry[1–5]. Erving *et al.*[6] observed early that the colour of primary mercuric dithizonate was changed from orange yellow to an intense royal blue upon exposure to light. It was later discovered that Reith and Gerritsma[5] had made the same observation a year earlier. They had noted that the change from blue to yellow took place immediately on shaking with aqueous acid and that the photometric effect was inhibited in the presence of 2N-acetic acid. The effect was rediscovered five years later by Webb *et al.*,[4] but the curious phenomenon was not followed up in depth until the American Cyanamide Company recognized its potential use in solar batteries, car wind screens, and sunglasses[7].

A large number of metal dithizonates were prepared by Meriwether *et. al.*,[7] who reported that none of the secondary dithizonates were found to be photochromic in solution. Of 24 primary dithizonates examined by them at room temperature and at –80°C; in 16 solvents, 9 were found to be photochromic under

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test condition with visible light. They also noticed that mercuric dithizonate was the only complex which exhibited photochromism in the solid state.

EXPERIMENTAL

Diphenylthiocarbazone

It was purified according to the method described by Erving *et al.*[8]

Primary Silver Dithizonate

It was prepared according to the method described by Meriwether, Breitner and Sloan[7]. The purity of complex was checked from determination of silver percentage in it by wet ashing of a known weight of complex by a mixture of perchloric and nitric acids followed by determination of silver in the resulting solution by means of atomic absorption spectometry. The percentage of silver in the complex amounts to 29.7%, which confirmed that the complex has the formula Ag(HDz).

Measuring Assembly

The measuring assembly used in our study on the variation of conductance of Ag(HDz) complex as a result of illumination with light of different wavelengths was composed of the following assembly. It consisted of 450 W Osram xenon arc lamp as an excitation source equipped with liquid filter to prevent heat from reaching the monochromator and affecting its dispersion. The monochromator used was Zeiss PMQII quartz prism one, having wavelength range from 185–2500 nm. The sample was placed in a double wall thermostatically controlled tight housing with an aperture facing the exit slit of the monochromator. The sample housing atmosphere was maintained humidity-free by putting sufficient amount of silica gel inside it. The photoconductivity of the samples were measured at constant D.C. voltage using the potential probe method.[9]

RESULTS AND DISCUSSION

The effect of light illumination on the molecular structure of primary silver dithizonate was monitored by the different changes in its electronic absorption spectrum, IR, and photoinduced current produced upon illumination.

It was found practically upon exposing primary silver dithizonate complex to illumination with different wavelengths in the range from ultraviolet (250 nm) to visible light (up to 600 nm) that a violet colouration (activated state) of complex was developed out. The original orange-red colouration of complex was retuned again in dark. The rate of return was found to depend primarily on temperature of complex sample.

At high levels of daylight illumination at 25°C, the time of return of activated violet complex to the normal orange-red form was found to be less than two minutes.[10]

It was noticed that the activated state was reached by monochromatic illumination at 273 or 462 nm after about 15 minutes at 5°C obviously from the variation of induced photocurrent values with current as showin in Fig. 1. The return time of the complex activated state to the normal one was found to be in the order of several hours.

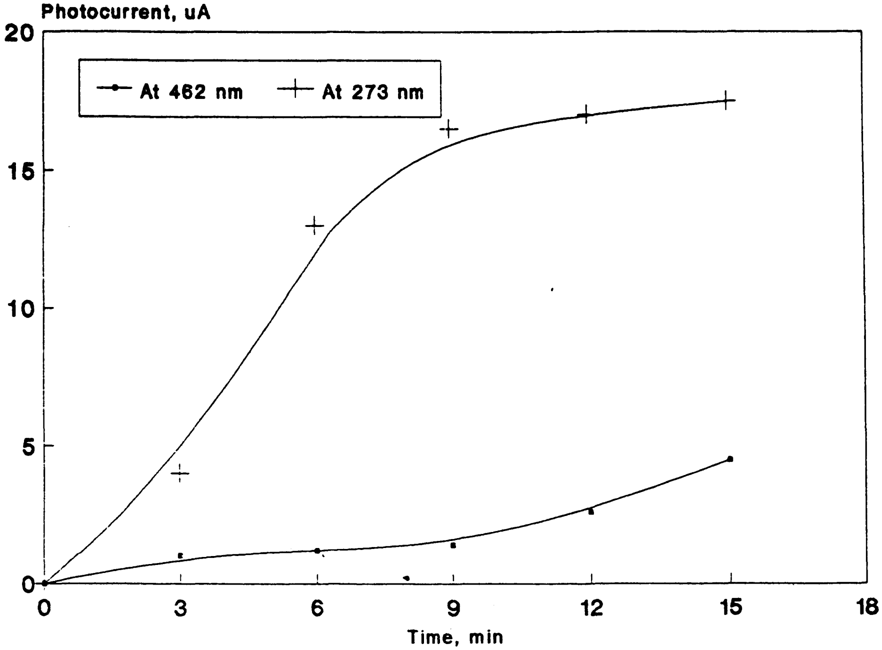
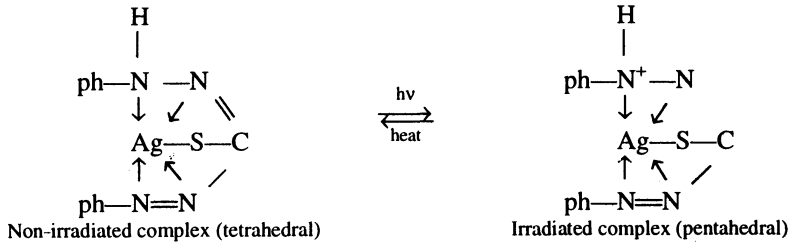


Fig. 1 Variation of photocurrent with time for primary silver dithizonate at different illuminations.

The variation of photoinduced current, produced upon illumination with monochromatic wavelengths, namely 273, 436, 250 and 600 nm, indicated that the highest current values were produced at the two former wavelengths. This may be attributed to the transformation of silver dithizonate complex to different possible activation states.

The transformation—as appeared from induced current values depends—on molecular extinction coefficient of excitation wavelengths. A number of possible structures of the activated states can be represented as follows:



The creation of partially or completely positive charge on one of the nitrogen atoms, due to probable formation of covalent bonding between it and silver ion instead of coordination one, upon illumination, leads to great increase in the induced photocurrent values as shown in Fig. 2. Upon illumination with wavelengths other than the above mentioned absorption peaks, the sample behaves as if it is kept in dark and also gives a very weak induced current (few nanoamperes) as shown in Fig. 3.

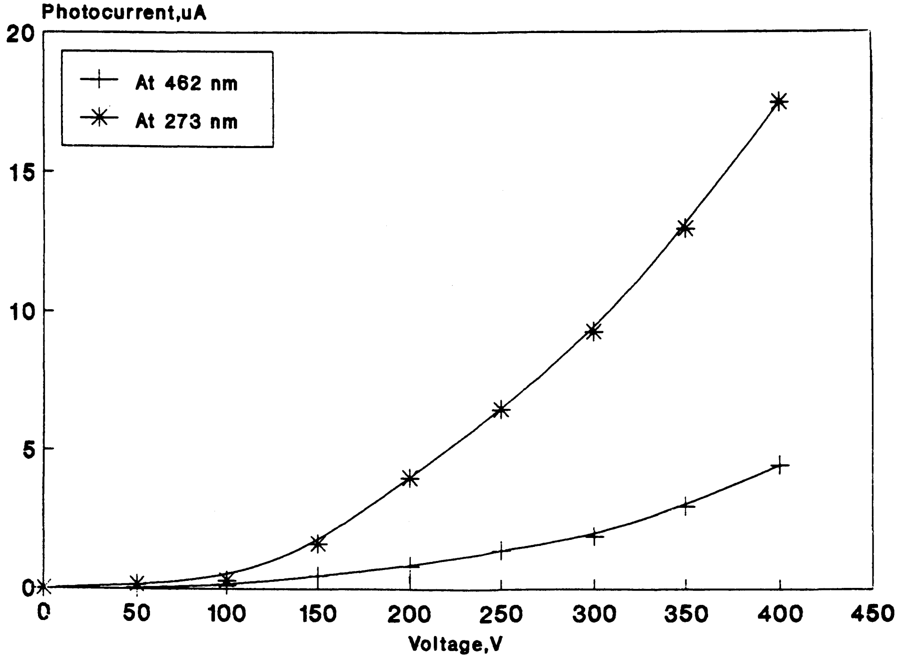


Fig. 2 Variation of photocurrent with applied voltage for primary silver dithizonate at different illuminations

There is a great change in both visible and ultraviolet spectra which may be attributed to the change of molecular structure of complex. It seems that the nonirradiated complex has the tetrahedral configuration whereas the irradiated one has a distorted square pyramidal structure. It is also concluded that the irradiated complex has bivalent silver ion as can be seen from gyrometric value of electron spin resonance (Fig. 4).

The dithizone ligand was found to exhibit no photochromic effect, *i.e.*, the current values of its sample did not show variation upon illumination at different wavelengths. This clarifies the importance of the role of complexation of dithizone with transition elements in promotion of transformation of normal molecule into activated state.

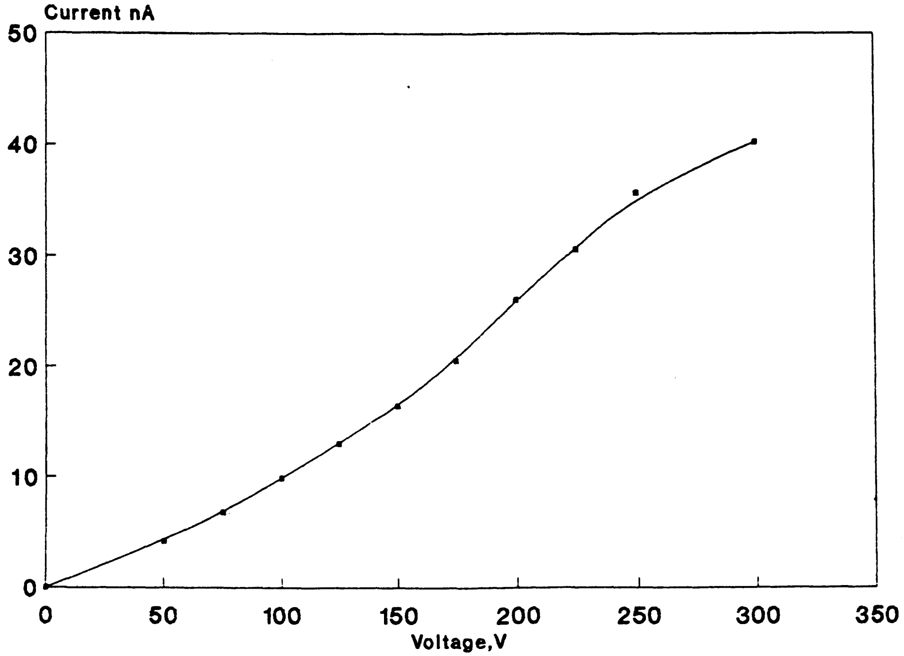


Fig. 3 Variation of current with applied voltage for dithizone at dark, 460 & 620 nm at 50.

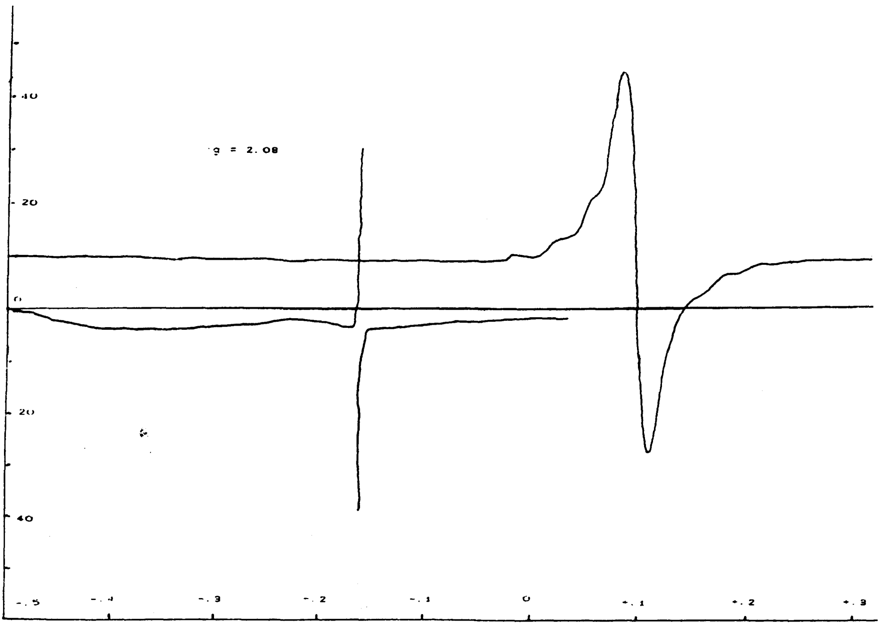


Fig. 4 ESR spectrum of irradiated primary silver dithizonate complex

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