

formed, using as sources a 750-w. tungsten source in a 35-mm. slide projector with a water filter (for the infrared radiation) plus a Corning 2-64 cut-off filter for wave lengths $>640\text{ m}\mu$ or a Corning 3-72 cut-off filter for wave lengths $>450\text{ m}\mu$. For the wave length range 300–360 $\text{m}\mu$, a 1000-w. high-pressure xenon arc light source was used in conjunction with a Corning 7-54 band-pass filter and a 1-cm. thickness of an aqueous solution containing 50 g./100 ml. of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$.

Photochemical Stability Studies. A GE BH-6 1000-w. high-pressure mercury arc source at a distance of 15 cm. was used for the stability studies. The dithizonate solutions to be tested (3.5 ml.) were sealed in identical 4-ml. Pyrex glass tubes. Twelve of these tubes were mounted on a drum which was mounted vertically and rotated slowly in front of the source. A maximum of three tubes of each solution was prepared and exposed for different periods. The per cent decomposition of the exposed samples was determined by comparing the optical density at the visible maximum with that of an unexposed portion of the same solution. The complexes decomposed to colorless or weakly absorbing

products. The following Corning filters were used along with a water filter for the different wave length regions: $>400\text{ m}\mu$, 3-73; $>360\text{ m}\mu$, 3-75; $>340\text{ m}\mu$, 0-52; $>320\text{ m}\mu$, 0-54.

Infrared spectra were determined in mineral oil mulls on a Perkin-Elmer Model 21 recording infrared spectrophotometer with sodium chloride optics. A Bausch and Lomb Spectronic 505 spectrophotometer was used for the ultraviolet and visible spectroscopy. Melting points were determined in an aluminum block and are uncorrected. Metal analyses on the complexes were done by X-ray emission. A Varian V-4500 electron spin resonance spectrometer was used for the e.s.r. experiment.

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Kinetic and Infrared Study of Photochromism of Metal Dithizonates

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Infrared and kinetic studies of the photochromism of $\text{Hg}(\text{HDz})_2$, $\text{Ag}(\text{HDz})$, and $\text{Bi}(\text{HDz})_3$ in solution at 25° and lower temperatures have been carried out. The thermal return reaction of $\text{Hg}(\text{HDz})_2$ in benzene at 25° follows first-order kinetics and also shows a direct linear dependence on total complex and water concentration. N-Deuteration of the complex produces a threefold decrease in the return rate. A structure is proposed for the activated form of $\text{Hg}(\text{HDz})_2$, and a mechanism for the return to the normal form is presented involving a cis-trans isomerization of an azomethine group and a rate-determining proton shift. $\text{Ag}(\text{HDz})$ and $\text{Bi}(\text{HDz})_3$ display behavior essentially identical with that of the mercury complex.

Introduction

In the preceding paper¹ we discussed the photochromic and photochemical behavior of a large number of metal dithizonates. In view of the unique characteristics of these photochromic systems, it is of interest to determine the structures of the activated forms of the complexes and the mechanisms of the reactions involved. To this end a technique has been developed for following the infrared spectral changes of the complex solutions under irradiation, and a kinetic study of

the return reaction of mercury and silver dithizonate has been carried out. Both the N-protonated and N-deuterated complexes have been examined. The results of these studies and their mechanistic consequences are the subject of this paper.

Results

Infrared Spectra. The infrared spectrum of $\text{Hg}(\text{HDz})_2$ in either carbon disulfide or carbon tetrachloride at -15° was essentially the same as that of the solid. Carbon disulfide was used as solvent for study of the region above 3000 cm^{-1} and below 1300 cm^{-1} , and carbon tetrachloride was used for the region above 3000 cm^{-1} and below 1700 cm^{-1} . The complex is much more soluble in carbon disulfide.

Significant changes were observed in the solution spectra under irradiation with visible light. Figure 1 shows the infrared spectra of the normal and activated forms of $\text{Hg}(\text{HDz})_2$ in carbon disulfide solution at two different concentrations. In the saturated solution only a partial conversion to the activated form was achieved, but the dilute solution was converted practically quantitatively to the activated form under the same experimental conditions. In Figure 2 the normal and activated spectrum of $\text{Hg}(\text{HDz})_2$ is shown in carbon tetrachloride solution. This result was obtained by using different cell thicknesses for the various bands of the spectrum.

(1) L. S. Meriwether, E. C. Breitner, and C. L. Sloan, *J. Am. Chem. Soc.*, **87**, 4441 (1965).

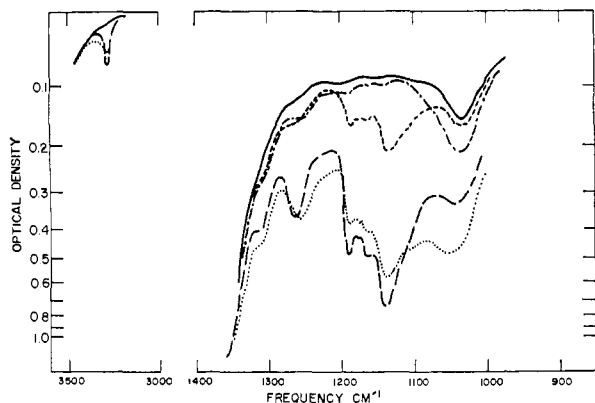


Figure 1. Infrared spectra of solutions of $\text{Hg}(\text{HDz})_2$ in carbon disulfide at -15° : —, solvent only; — —, saturated solution, unirradiated;, saturated solution, irradiated; - - - -, dilute solution (1:4 from saturated), unirradiated; - . . ., dilute solution, irradiated (cell thickness, 6 mm.; air in reference beam).

Figures 1 and 2 together supply the complete spectrum of activated $\text{Hg}(\text{HDz})_2$ and also confirm the reproducibility of the results and their solvent independence. All of the above-described spectral changes were reversible. The infrared spectrum obtained after complete return was identical with that of the starting material. The solutions were also checked for reversibility by visible spectroscopy. The changes in the infrared spectra under irradiation corresponded to the visually observed color changes of the solutions.

The important infrared bands of the normal and activated forms of $\text{Hg}(\text{HDz})_2$ are listed in Table I. In the activated form the N-H stretching mode moves

Table I. Wave Numbers (cm^{-1}) of Significant Infrared Bands of the Normal and Activated Forms of $\text{Hg}(\text{HDz})_2$ and $\text{Hg}(\text{DDz})_2$ in CS_2 and CCl_4 Solution at -15°

	$\text{Hg}(\text{HDz})_2$		$\text{Hg}(\text{DDz})_2$	
	Normal	Acti- vated	Normal	Acti- vated
N-H stretch	3280	3340	~ 2400 (N-D)	2470 (N-D)
N-H bend	1535	1510
N-Ph	1365	1350	1378	1350
N-C-S	1190	1050	1182	1130
	1175		1175	1010
	1165		1167	
	1140		1142	

to higher and the N-H bending mode shifts to lower frequencies, the result of the formation of a weaker hydrogen bond.² There is also a small shift in the N-Ph band from 1365 to 1350 cm^{-1} and a very significant change in the group of four absorption bands between 1100 and 1200 cm^{-1} , which represent the coupled N-C-S bond vibrations. As shown in the spectra, this whole group of bands disappears in the activated form, giving rise to one new band at 1050 cm^{-1} .

The N-deuterated complex, $\text{Hg}(\text{DDz})_2$, served to identify some of the bands in the infrared spectrum of $\text{Hg}(\text{HDz})_2$ and confirm the identity of others. It also

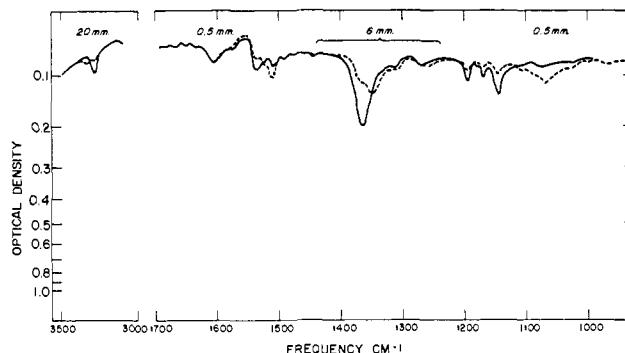


Figure 2. Infrared spectra of saturated solutions of $\text{Hg}(\text{HDz})_2$ in carbon tetrachloride at -15° : —, unirradiated; - - -, irradiated (cell thickness, 0.5, 6.0, 20 mm.; solvent only in reference beam).

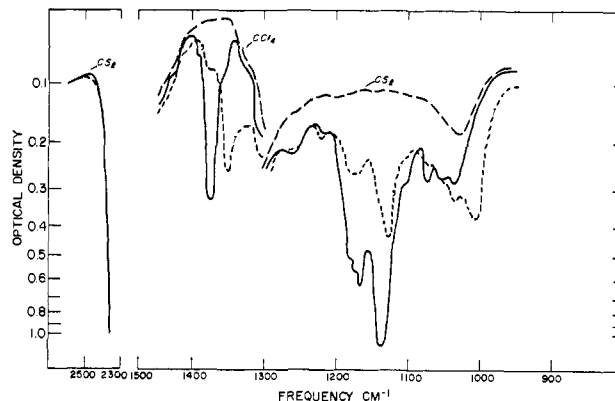


Figure 3. Infrared spectra of saturated solutions of $\text{Hg}(\text{DDz})_2$ in carbon disulfide and carbon tetrachloride at -15° : - - -, solvent only; —, unirradiated; - . . ., irradiated (cell thickness, 6 mm.).

provided valuable information regarding the mechanism of the reaction during the kinetic measurements. The infrared spectra of the normal and activated forms of $\text{Hg}(\text{DDz})_2$ in carbon disulfide and carbon tetrachloride at -15° are shown in Figure 3, and the band frequencies are summarized in Table I. The N-D stretching frequency (2400 cm^{-1}) in the normal form has replaced the N-H stretching band. The N-D bending mode is not observable; it probably moved down to lower frequencies where it interacted with other vibrational modes. The other bands are all present, only slightly shifted from those of the undeuterated compound.

The activated form of the deuterated compound shows changes in the infrared similar to those observed in the undeuterated one. It was difficult to follow the change in the N-D stretching band because in solution it appears as a shoulder on a carbon disulfide band. The shift is in the same direction, however, the new band appearing at 2470 cm^{-1} . A corresponding lowering of the N-Ph band to 1350 cm^{-1} occurs. The four bands of the N-C-S group give way to two new bands at 1130 and 1010 cm^{-1} . The appearance of two new bands in the activated form compared with the one band in $\text{Hg}(\text{HDz})_2$ may be due to interaction with the N-D bending mode which is in the same region.

(2) J. F. Duncan and F. G. Thomas, *J. Chem. Soc.*, 2814 (1960).

It was observed during these experiments that deuteration of the mercury dithizonate slowed down the return rate of the activated form by a factor of about three. From the infrared spectra, deuteration occurred instantaneously upon the addition of D₂O to a benzene solution of the complex.

The changes in the infrared spectrum of a carbon disulfide solution of Bi(HDz)₃ under irradiation were also studied. Because of its very fast return rate only a 10–15% conversion to the activated form was achieved under the experimental conditions (–80°). However, this was sufficient to confirm at least qualitatively that the changes occurring in the infrared spectrum of Bi(HDz)₃ are analogous to those observed in Hg(HDz)₂ under irradiation. In the activated form of Bi(HDz)₃, the N–H stretching mode moves to higher frequency and the group of N–C–S bands diminishes while a new band appears at lower frequency.

Kinetic Studies. Hg(HDz)₂ in benzene solution was chosen as a model for the kinetic studies on photochromic dithizonates because the rate of return of this system is measurable at room temperature. The return reaction was followed spectrophotometrically both by the disappearance of the absorption band of the activated form at 605 mμ (ϵ 3.9 × 10⁴) and by the reappearance of the 490-mμ (ϵ 7.0 × 10⁴) band of the normal form. Pseudo-first-order rate constants calculated from these two measurements agreed within experimental error, proving that the 490- and 605-mμ compounds were the only species present in the system in measurable concentration. Further evidence for the presence of only two components in the system was the appearance of an isosbestic point at 540 mμ.¹

The rate of return of Hg(HDz)₂ in benzene solution follows first-order kinetics. However, the rate constant was found to be a function of (1) the total concentration of complex, (2) the water content, and (3) (in solutions allowed to stand in contact with water) the time elapsed since preparation of the solution. The rate constants are listed in Table II.

Table II. Rate Constants for the Return Reaction of Mercury and Silver Dithizonates

Run no.	Complex	Concn., M × 10 ⁵	Sol-vent ^a	Water concn., M	Temp., °C.	k _{obsd} × 10 ² , sec. ⁻¹
22	Hg(HDz) ₂	1.26	B	0.039	25	1.94
23	Hg(HDz) ₂	1.26	B	0.039	25	1.72
34	Hg(HDz) ₂	2.04	B	0.039	25	4.40
35	Hg(HDz) ₂	0.74	B	0.039	25	2.07
36	Hg(HDz) ₂	0.34	B	0.039	22	1.17
42	Hg(HDz) ₂	1.04	B	0.039	25	2.94
43	Hg(HDz) ₂	1.09	B	0.00	25	0.27
44	Hg(HDz) ₂	1.07	B	0.020	25	1.06
45	Hg(HDz) ₂	1.09	B	0.013	25	0.77
46	Hg(HDz) ₂	1.06	B	0.026	25	1.24
47	Hg(HDz) ₂	1.40	B	0.000	25	0.13
49	Hg(HDz) ₂	0.43	B	0.00	25	0.15
50	Hg(HDz) ₂	0.43	B	0.039	25	0.67
51	Hg(DDz) ₂	0.43	B	0.039 ^b	25	0.25
53	Ag(HDz)	2.93	T	0.00	11.5	1.08
54	Ag(HDz)	2.63	T	0.39	11.5	6.59
55	Ag(DDz)	2.70	T	0.39 ^b	11.5	2.42

^a B = benzene, T = tetrahydrofuran. ^b 99.7% D₂O.

Because of the dependence of the return rate on the water concentration, most measurements were made on

solutions saturated with water by allowing them to equilibrate by standing over water for 15–20 hr. in a 25° thermostat. The solubility of water in benzene at 25° is 0.039 M.³ The return rates of these solutions decreased in proportion to the time they remained in contact with the aqueous phase. Once the solution was separated from the aqueous phase, no matter whether at once or after many hours, the return rate then was constant and did not change with time. The reproducibility of experiments carried out under these conditions was verified by carrying two solutions of identical Hg(HDz)₂ concentration through the above water treatment and measuring their rates of return. The k_{obsd} of the two reactions agreed within the experimental error (runs 22 and 23, Table II). These effects were probably due to a slow hydrolysis of the mercury complex while the benzene solution was in contact with the water layer. This would be expected to decrease the return rate because of its dependence on total complex concentration.

The effect of initial concentration of Hg(HDz)₂ was ascertained by measuring the return rates of three solutions whose complex concentrations ranged from 3.4 × 10⁻⁶ to 2.0 × 10⁻⁵ M (runs 34–36, Table II). First-order plots of these reactions were strictly linear, but the rate was found to increase with increasing complex concentration. A plot of k_{obsd} vs. initial concentration (Figure 4) was a straight line, indicative of a linear rate dependence on total complex concentration.

A similar effect of water concentration on the return rate was found. The rate also increased with increasing water concentration (runs 42–47, Table II), and a plot of k_{obsd} vs. water concentration at constant total complex concentration (Figure 4) was again linear. The plot of k_{obsd} vs. complex concentration (Figure 4) also fails to go through the origin, which is further indication of a water-dependent process. The “dry” benzene run (43) was arbitrarily assigned a water content of 0.00%. In order to determine whether there was a true water-free term in the rate expression, a rigorously dried solution of the complex in benzene was prepared in a vacuum system and sealed off in a spectrometer cell. The return rate of this sample (run 47) was only 50% lower than that of the “dry” benzene run. The k_{obsd} obtained in the absence of water was 3.2% of the k_{obsd} in water-saturated benzene. The presence of water is therefore not essential to the return process.

Comparison of the return rates of a water saturated and a deuterium oxide saturated solution of Hg(HDz)₂ in benzene at the same initial concentration (runs 49–51, Table II, and Figure 5) shows that deuteration of the complex slows down the reaction by a factor of 2.8. This is in good agreement with the factor of about three observed in the infrared experiments.

In order to test the validity of the above results for other photochromic dithizonates, the return rate of Ag(HDz) in tetrahydrofuran was also measured (runs 53–55, Table II). Because of the fast return of this system at room temperature, the rates were determined at 11.5 ± 0.5°. In Figure 6 the return rates of three 2.7 × 10⁻⁵ M solutions of Ag(HDz) in tetrahydrofuran are plotted as first-order reactions. Solution I was

(3) "International Critical Tables," Vol. III, E. W. Washburn, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 389.

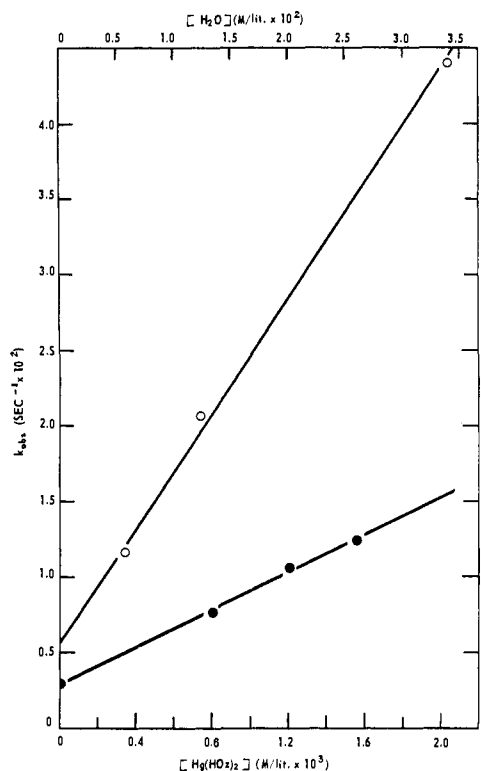
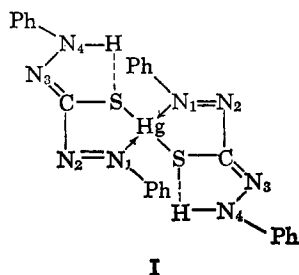


Figure 4. Plots of k_{obsd} vs. $[\text{Hg}(\text{HDz})_2]$ at constant water concentration ($3.9 \times 10^{-2} M$, open circles, bottom scale) and of k_{obsd} vs. $[\text{H}_2\text{O}]$ at constant $\text{Hg}(\text{HDz})_2$ concentration ($1.08 \times 10^{-5} M$, solid circles, top scale) in benzene at 25° .

dry, solution II contained 0.7% H_2O , and solution III contained 0.7% D_2O . These results show that the return reaction (1) follows first-order kinetics, (2) is accelerated by water, and (3) is slowed down by deuteration. From a comparison of k_{obsd} for solutions II and III, deuteration slows down the reaction by a factor of 2.9, essentially the same as in the $\text{Hg}(\text{HDz})_2$ system.

Discussion

Comparison of infrared spectra of solid $\text{Hg}(\text{HDz})_2$ with those of its solutions shows that the same structural form is present in unirradiated solution as in the solid state. On the basis of an X-ray crystallographic study⁴ of $\text{Hg}(\text{HDz})_2$ crystals containing pyridine of crystallization and the similarity of the infrared spectra of pure $\text{Hg}(\text{HDz})_2$ and the $\text{Hg}(\text{HDz})_2$ -pyridine crystals, we feel justified in assigning structure I to $\text{Hg}(\text{HDz})_2$ in both the pure solid state and in solution. In I the hydrogen bond is from N_4 to S instead of the nitrogen atom of pyridine, as found in the solvated



(4) M. M. Harding, *J. Chem. Soc.*, 4136 (1958).

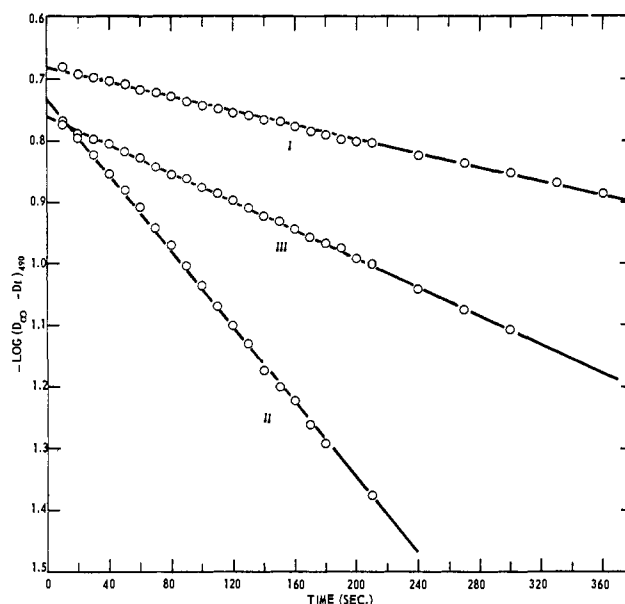


Figure 5. Effect of H_2O and D_2O on the return reaction of $\text{Hg}(\text{HDz})_2$ in benzene at 25° : I, $4.3 \times 10^{-6} M \text{Hg}(\text{HDz})_2$, dry; II, $4.3 \times 10^{-6} M \text{Hg}(\text{HDz})_2$, $3.9 \times 10^{-2} M \text{H}_2\text{O}$; III, $4.3 \times 10^{-6} M \text{Hg}(\text{DDz})_2$, $3.9 \times 10^{-2} M \text{D}_2\text{O}$.

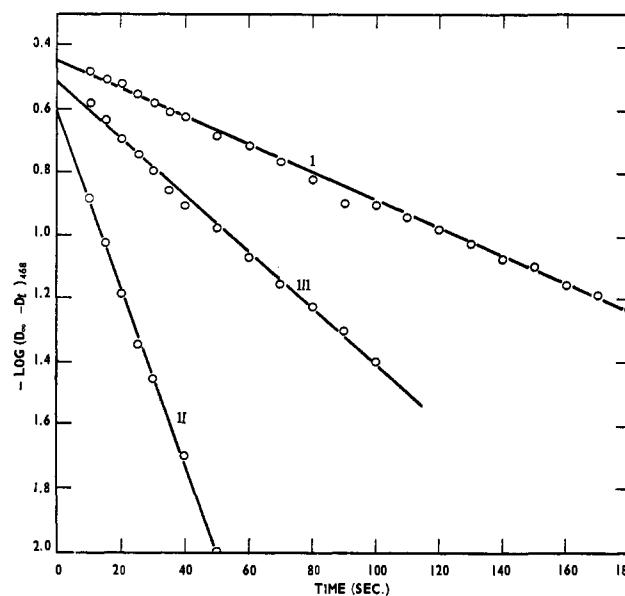


Figure 6. Effect of H_2O and D_2O on the return reaction of $\text{Ag}(\text{HDz})_2$ in tetrahydrofuran at 11.5° : I, $2.9 \times 10^{-5} M \text{Ag}(\text{HDz})_2$, dry; II, $2.6 \times 10^{-5} M \text{Ag}(\text{HDz})_2$, $0.39 M \text{H}_2\text{O}$; III, $2.7 \times 10^{-5} M \text{Ag}(\text{DDz})_2$, $0.39 M \text{D}_2\text{O}$.

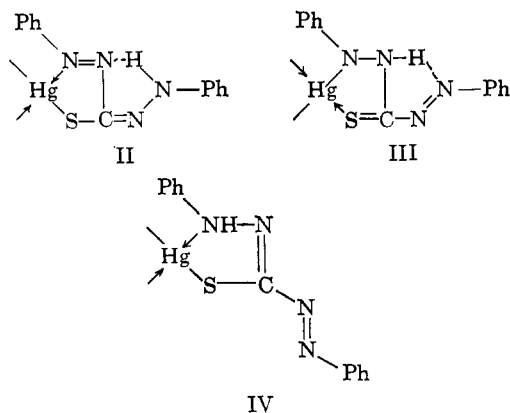
crystals. Infrared results indicate a strongly hydrogen-bonded $-\text{NH}$ in the inactive form of $\text{Hg}(\text{HDz})_2$. The $\text{S} \cdots \text{H}-\text{N}$ hydrogen bond is strengthened in I by the possibility of several possible resonance structures of the molecule with a negative charge on the sulfur atom as well as the strong polarization of the mercury-sulfur bond.

Since no over-all chemical change has occurred in the photochromic process and the interconversion involves no long-lived reaction intermediates, the activated form of $\text{Hg}(\text{HDz})_2$ must be assumed to be either an isomer of the normal form or a product

formed by the reversible dissociation of the normal form. A dissociation-recombination route appears to be ruled out since the spectrum of free dithizone or its anion has never been observed in solutions containing over 80% of the complex in the activated form. The fast return rates at high dilution are also inconsistent with a recombination process. In addition, the very high stability of the complex would prevent dissociation.

From spectral evidence, the activated form has a weakly hydrogen-bonded -NH group and significant changes in the conjugated chromophore causing a large shift of the normal visible absorption band and also major changes in the NCS region of the infrared spectrum. Inasmuch as these spectral changes are independent of the metal atom, the number of dithizone ligands attached thereto, and the degree of conversion to the activated form, we must assume that the associated structural changes occur in each ligand independently of its neighbors in the complex.⁵ Therefore, we will restrict our discussions of mechanism to one ligand-metal chelate ring system.

Structures II, III, and IV are all consistent with the infrared properties of the activated form. II can be



derived from I by the cleavage of the hydrogen bond to the sulfur, a *cis-trans* isomerization around the C=N bond, and the formation of a new hydrogen bridge to N₂. This would be a weaker hydrogen bond than that in I because of the low basicity of the azo nitrogen. Structure III can be arrived at in the same way as II except that the hydrogen atom is completely transferred from N₄ to N₂ resulting in a hydrogen bond to N₄. This produces a drastically altered chromophore containing a thiocarbonyl group. Many organic compounds having this structure in a conjugated system are known to be blue,⁶ having visible absorption bands in the same region (580–605 mμ) as the activated form of Hg(HDz)₂.

The photochemical I → IV structural change could occur in two different ways: (1) cleavage of the Hg-N₁ bond followed by rotation of the ligand about the C-S bond and formation of a new linkage between Hg and N₄; (2) transfer of a hydrogen atom from N₄ to N₁ accompanied only by electron shifts. This latter process might require the presence of an auxiliary

proton donor-acceptor to facilitate the hydrogen transfer.

The information obtained from the kinetics of the return reaction of Hg(HDz)₂ serves to eliminate I → II and route 1 of the I → IV process. This follows from the fact that the return rate of the N-deuterated compound is about one-third that of the undeuterated material; hence, the rate-determining step must involve a proton transfer. Neither I → II nor route 1 to IV requires a proton shift.

The rate expression derived from the kinetic studies provides additional support for the assignment of structure III to the activated form. The results can be fitted to the following equation

$$V = k_1(\text{H}_2\text{O})C_T C_t + k_2 C_T C_t + k_3(\text{H}_2\text{O})C_t$$

where C_T = total concentration of dithizonate complex, C_t = concentration of activated form at time t , and k_1, k_2, k_3 = constants. The first term arises from the observed linear dependence of the return rate on the initial concentration of complex and water in the system. A water-free process and a route independent of total complex are also operative, however, since experiments on rigorously dried systems still show a slow but measurable return rate and the k_{obsd} vs. complex concentration plot (Figure 4) has a positive intercept at zero complex. These reactions are represented by the second and third terms, respectively, of the rate equation.

The dependence of the return rate on the concentration of water and complex can be explained by assuming that they participate in the reaction as proton-transfer agents within a hydrogen-bonded aggregate of perhaps several complex and water molecules. The solvent may also serve in this role. The very rapid deuterium exchange of the complex and the observed pH and solvent sensitivity of the photochromic reaction¹ support this hypothesis.

Although, on kinetic grounds alone, IV (*via* route 2) would appear to be an equally good choice to III for the activated form, since it satisfies the requirement of a proton shift and the need for a proton carrier in the return reaction, the change in chromophore is not enough to account for a 100–120-mμ shift toward longer wave lengths in the visible absorption band.

Structure III best satisfies the collected results from kinetics and infrared and visible spectroscopy. Its return to I requires a proton shift, and it is reasonable that this process is mediated by a proton donor or acceptor and would be slow in the absence of such promoters. It may be argued that in the nonphotochemical III → I process the *cis-trans* isomerization about the C=N group should be the slow rate-determining step and the proton transfer should be very fast. However, it has been shown recently by Curtin and Hausser⁷ that isomerization about azomethine groups can be very fast, and intermolecular proton transfer in dilute solution in aprotic and nonpolar solvents has been found to be relatively slow.⁸ It is entirely possible that the return reaction in polar solvents follows different kinetics in which the *cis-trans*

(5) Spectral evidence suggesting the possibility of ligand-ligand interaction through the metal atom was found only in the planar complexes of Ni, Pd, and Pt.¹

(6) P. Brocklehurst and A. Burawoy, *Tetrahedron*, **10**, 118 (1960).

(7) D. Y. Curtin and J. W. Hausser, *J. Am. Chem. Soc.*, **83**, 3474 (1961).

(8) C. G. Swain, J. T. McKnight, and V. P. Kreiter, *ibid.*, **79**, 1088 (1957).

shift now becomes the slow step. Further evidence on this point must await flash photolysis studies which have not yet been carried out.

In the absence of evidence to the contrary, it must be assumed that under the conditions of this study no direct intramolecular hydrogen transfer from N_2 to N_4 in fact occurs. A water molecule or a second molecule of complex or both must serve as a proton bridge. The activated complex for this reaction is probably a complex structure consisting of several water and dithizonate molecules bound together by hydrogen bonds. Unfortunately, molecular weight measurements to determine the degree of polymerization of the dithizonate in solution are prevented by low solubility.

The great similarity in behavior of the monodithizonate of silver, the bisdithizonate of mercury, and trisdithizonate of bismuth lends considerable support to the hypothesis that the above mechanism is common to the photochromism of metal dithizonates. The results obtained with the silver dithizonate system are of additional significance. In the above discussion, only one-half of the $Hg(HDz)_2$ molecule was considered; the possibility of interaction between the two ligands of the same complex molecule was neglected. The kinetic study of the $Ag(HDz)$ system seems to justify this treatment by its similarity to $Hg(HDz)_2$. In the latter system under illumination the presence of the following three species is inferred: $Hg(HDz)_2$, $Hg(HDz)(HDz^*)$, and $Hg(HDz^*)_2$ (where HDz and HDz^* refer to ligand structures in I and III, respectively), their relative proportion depending upon the light level, temperature, etc. However, these are kinetically and spectroscopically indistinguishable from a mixture of $Hg(HDz)_2$ and $Hg(HDz^*)_2$ having the same ratio of HDz to HDz^* . Therefore, for the present we must be content with the assumption that the photochromic process in metal dithizonates occurs in each ligand independently and is unaffected by the presence of a second or third dithizone ligand attached to the same central metal.

Experimental Section

Materials. $Hg(HDz)_2$, $Bi(HDz)_3$, and $Ag(HDz)$ were prepared as described previously.¹

$Hg(DDz)_2$. A benzene solution of $Hg(HDz)_2$ was shaken successively with several portions of 99.7% D_2O (Merck Sharp and Dohme, Canada). The benzene layer was then evaporated to dryness under vacuum. By infrared analysis of the N-H and N-D stretching bands the compound was found to be 85% N-deuterated. For the infrared studies this compound was dissolved in carbon disulfide or carbon tetrachloride which had been previously saturated with D_2O . Infrared analysis of these solutions revealed that the complex was now >99% N-deuterated.

For the kinetic studies $Hg(DDz)_2$ was prepared by shaking a dry benzene solution of $Hg(HDz)_2$ three to four times with fresh portions of 99.7% D_2O and allowing the solution to stand over D_2O overnight.

Solvents. Benzene used for the kinetic measurements was prepared by distilling reagent grade benzene from sodium and discarding the first portion of the distillate. Tetrahydrofuran was purified by distillation from calcium hydride followed by passing it

through a column of Woelm neutral alumina. Carbon tetrachloride and carbon disulfide used in the infrared experiments were taken directly from freshly opened bottles of reagent grade material.

Infrared Study. A Perkin-Elmer Model 21 automatic recording infrared spectrophotometer with sodium chloride optics was used for the infrared measurements. It was necessary to measure the spectra of the activated forms of the complexes during irradiation of the solutions at low temperature. For this reason a special cell holder was used in this study similar in design to that described by Wagner and Hornig⁹ for low-temperature infrared work. The dithizonate solution was contained in a tightly stoppered commercial sodium chloride cavity cell having a cavity cross section of 6×4 mm. and polished on all four outer faces. This cell was attached to the copper block extension of the coolant reservoir such that the infrared beam passed through the 4-mm. face of the cavity and an intense visible light source was focused on the 6-mm. face perpendicular to the infrared beam.

To avoid fogging, the cell holder was evacuated before the Dry Ice-acetone cooling mixture was added to the center well. The temperature was controlled by varying the amount of Dry Ice in the freezing mixture.

Kinetic Study. This work was carried out in a Bausch and Lomb Spectronic 505 ultraviolet-visible spectrophotometer equipped with a specially designed constant temperature cell holder which permitted external irradiation of the sample. This cell holder was similar in design to that described by Kuhn and Weitz¹⁰ except that the body of the cell holder was a solid brass block, drilled and plugged for the circulating coolant; the sample chamber was provided with a magnetic stirrer; and the whole device fitted inside the sample compartment of the Bausch and Lomb spectrometer. Temperature control in the cell holder was maintained by circulating absolute ethanol from a constant temperature bath.

Pseudo-first-order rate constants for the return of mercury dithizonate were obtained from the expression

$$k_{\text{obsd}} = \frac{2.303}{t} \log \frac{D_0}{D_t - D_\infty}$$

in which D_0 , D_t , and D_∞ refer to the corrected optical densities at 605 $m\mu$ at the beginning of the run, time t , and after complete return, respectively, and the corresponding expression

$$k_{\text{obsd}} = \frac{2.303}{t} \log \frac{(D_\infty - D_0)}{(D_\infty - D_t)}$$

in which D_0 , D_t , and D_∞ now refer to optical densities measured at 490 $m\mu$. First-order plots were linear to >90% conversion. The average deviation of the calculated rate constants was $\pm 2-5\%$. Duplicate runs agreed to within 6%. No variation was observed in the rate constant as a function of the degree of conversion of complex to the activated form at t_0 over a range of 10-80% initial activated form.

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The light source used in all experiments was a General Electric Projection DDB, 115–120 v., 750-w. bulb housed in a standard manual 35-mm. slide projector. A Corning No. 3387 filter and 4 cm. of distilled water in a Pyrex glass cell were used to absorb

radiation below 450 m μ and above 1000 m μ , respectively.

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A Proton Magnetic Resonance Study of Some Dialkylaminophosphorus Derivatives

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Chemical shift and P^{31} -H coupling constant data have been obtained for 24 dimethylamino- and diethylamino-substituted phosphorus compounds. The P^{31} -H coupling constants of the diethylaminophosphines were also determined by $H^1[H^1]$ double resonance. In general, increasing the covalency of the phosphorus atom by addition of oxygen or sulfur, or replacement of R_2N -groups by halogen atoms, increases the magnitude of J_{PNCH} and simultaneously decreases the τ value of the N-methyl or N-methylene protons. Examination of the spectra of three aminophosphine-methiodide adducts has established that it is only the phosphorus atoms that are quaternized. The preparation of three new phosphorus-nitrogen compounds is described.

Introduction

Most of the n.m.r. studies that have been carried out on phosphorus compounds have involved the determination of P^{31} chemical shifts.^{1,2} Although it is possible to determine spin-spin coupling constants from P^{31} n.m.r. spectra,^{1,2} more accurate values can sometimes be obtained from the n.m.r. spectra of other nuclei, particularly when the magnitude of the coupling is small. Recent proton magnetic resonance studies³⁻⁶ of organophosphorus compounds have yielded some useful data on chemical shifts and P^{31} -H coupling constants. In some cases⁷⁻¹² the relative signs of the P^{31} -H coupling constants have been reported, although these have not been related to the C^{13} -H

coupling constant over one chemical bond which is commonly taken as a reference.

Most of the work cited above refers to compounds in which the phosphorus atom is attached to alkyl groups or hydrogen atoms. In this study we report on the effect of inserting a nitrogen atom between the alkyl group and the phosphorus atom. We were also interested in the extent to which nitrogen lone pairs are involved in π -bonding to phosphorus, and the effect of the charge and covalency of the phosphorus atom on the P^{31} -H coupling constants and H^1 chemical shifts. The n.m.r. spectra of some of the compounds have been reported previously^{13,14} (see also Tables I and II).

Table I. N.m.r. Data for Dimethylaminophosphines

Compd. no.	Compound	$\tau_{CH_3(N)}$	$\tau_{CH_3(P)}$	J_{PNCH}	J_{PCH}
1 ^a	$[(CH_3)_2N]_3P$	7.57	...	8.82	...
2 ^a	$[(CH_3)_2N]_3P(O)$	7.42	...	9.47	...
3 ^a	$[(CH_3)_2N]_3P(S)$	7.40	...	11.01	...
4	$[(CH_3)_2N]_2P(Cl)$	7.35	...	12.33	...
5	$[(CH_3)_2N]_2P(O)Cl$	7.32	...	12.87	...
6	$[(CH_3)_2N]_2P(S)Cl$	7.31	...	15.27	...
7 ^a	$(CH_3)_2NP(Cl)_2$	7.18	...	13.03	...
8 ^a	$(CH_3)_2NP(O)Cl_2$	7.13	...	15.87	...
9 ^a	$(CH_3)_2NP(S)Cl_2$	7.01	...	17.69	...
10 ^a	$[(CH_3)_2N]_2PCH_3$	7.37	8.86	8.73	7.49
11 ^a	$(CH_3)_2NP(CH_3)_2$	7.53	9.01	9.77	5.55

^a N.m.r. data reported previously. See ref. 13 for compounds 1, 2, 3, 7, 8, 9; and ref. 14 for compounds 1, 10, 11.

However, since several of these spectra were determined at 25 Mc.p.s. it was decided to rerun the compounds at 60 Mc.p.s. in the hope of measuring the coupling constants more accurately.

Experimental Section

The compounds of general formula $(R_2N)_3P$, $(R_2N)_2P(Cl)$, and $R_2NP(Cl)_2$ were prepared by treatment of

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