transition involving the unshared pair of electrons on the nitrogen. Bands of this type are expected to be solvent dependent; solvent effects on the spectra of pyridine and diazines have been found,[28] lending support to Kasha's assignment. The shoulders observed here were most evident in the diamagnetic acetylacetonates and in CuA_2, and in these cases lay in the 300–320 mμ region. These shoulders show little or no solvent dependence either in intensity or position. However, the shoulder in the CuA_2 spectrum completely disappears when the compound is measured in a solution of 40% CH_3NH_2 in H_2O, an effect similar to that observed in the spectra of certain carbonyl compounds in aqueous solution[29] where the intensities of the $n \rightarrow \pi^*$ transitions diminish, presumably due to solvent interactions with the non-bonding electrons. In any event, solvent effects may be diminished in the acetylacetonates by partial shielding of the ring oxygens by neighboring $-CH_3$ groups so that failure to observe them does not constitute firm evidence against the n-π^* assignment.

We have no direct evidence concerning the possibility of singlet-triplet transitions of the π-electrons in the chelate ring system. Evans[30] and others have identified singlet-triplet absorption bands in benzene and other aromatic hydrocarbons by perturbing the triplet state with the inhomogeneous field of the paramagnetic oxygen molecule. In the acetylacetonates, the paramagnetic metal ion, intimately associated with the π-system, might have been expected to accomplish a similar enhancement of the intensity. In the paramagnetic complexes, except for those of Cu(II) and VO(IV), no very pronounced shoulder is present on the long wave length side of the main absorption band and a number of smaller bands are present at longer wave lengths. However, we have been unable to distinguish these bands as either $n \rightarrow \pi^*$, singlet-triplet, or, in some cases, ligand field absorptions.

Finally, we have investigated three complexes of the lower transition series, Rh(III), Pd(II), Pt(II). These spectra fit into none of the above classes and are indeed a great deal richer. The three spectra are somewhat similar, all showing their most intense band at 240–250 mμ and a less intense band at ~300 mμ. In addition other less intense bands are observed in the region 260–290 mμ.

Acknowledgment.—Thanks are due to Mr. R. W. Fessenden for obtaining the proton resonance spectra.

CAMBRIDGE, MASS.

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[28] F. Halverson and R. C. Hirt, *J. Chem. Phys.*, **19**, 711 (1951); H. P. Stephenson, *ibid.*, **22**, 1077 (1954); R. J. L. Andon, J. D. Cox and E. F. G. Herington, *Trans. Faraday Soc.*, **50**, 918 (1954).

[29] F. A. Matsen, *J. Chem. Soc.*, 662 (1957).

[30] See D. F. Evans, *ibid.*, 1351, 3885 (1957), and references therein.

[CONTRIBUTION FROM HALL LABORATORY OF CHEMISTRY, WESLEYAN UNIVERSITY]

Chelates of Violuric Acid

BY PETER A. LEERMAKERS AND WILLIAM A. HOFFMAN

RECEIVED MARCH 8, 1958

An investigation of the coördinating properties of violuric acid has indicated that the reagent forms chelates with Fe(II), Fe(III), Cu(II) and Co. From the evidence presented Co is probably trivalent. The coördinating species was indicated to be a univalent violurate ion. Chelate species of 1,3-dimethylvioluric acid were found to be identical in their visible spectra over the *p*H range 3–7 with those of violuric acid. The stabilities of the violurate chelates are discussed and structures are proposed for them. A colorimetric method for copper utilizing violuric acid was developed.

Introduction

Violuric acid, the 5-oxime of alloxan, is known to exist as a mixture of keto–enol tautomers (Fig. 1).[1] Morton and Tipping[2] cite its *pK* as 4.7 and we have substantiated this value. Welcher[3] mentions the possibility of violuric acid as an analytical reagent for chromatographic separation of cations, but does not discuss its coördinating properties. Kuster[4] discusses the reaction of ferrous iron with violuric acid and, we believe, formulates the resultant species incorrectly. Hantzsch[5] reports violurate salts but does not refer to any violurate complexes. Aside from Kuster's work, no structural formulations have been attempted regarding the metal ion–violurate products. Coördination presumably occurs through the oxime functions (either the oxime or nitroso form) since the metal ion reactions of violuric acid are quite different from those of alloxan.

Since no thorough study was indicated, the authors decided to investigate violuric acid as a coördinating reagent. Spectrophotometric and polarographic studies were employed to determine formulas, stabilities, oxidation states (in case of cobalt) and, by deduction, structures of the metal chelates.

Experimental

Materials and Apparatus. Chemicals—Violuric acid, supplied by Eastman Kodak Co. and du Pont Co., was used as furnished, as was the dimethylurea and ethyl malonate used in the synthesis of 1,3-dimethylvioluric acid. Solutions of the metal ions, all sulfates, were prepared from recrystallized salts. Iron and copper solutions were standardized titrimetrically by the dichromate and thiosulfate methods, respectively. Cobalt solutions were standardized by the perborate method, with subsequent titration with thiosulfate.[6] All other chemicals were J. T. Baker analyzed reagents.

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[1] N. Chatak and S. Dutt, *J. Indian Chem. Soc.*, **5**, 665 (1928).

[2] R. A. Morton and A. H. Tipping, *J. Chem. Soc.*, **127**, 2541 (1925).

[3] F. Welcher, "Organic Analytical Reagents," Vol. 1, D. Van Nostrand Co., New York, N. Y., p. 193.

[4] W. Kuster, *Hoppe Seyler's Z. physiol. Chem.*, **155**, 173 (1926).

[5] A. Hantzsch, *Ber.*, **42**, 987 (1909).

[6] E. H. Swift, "A System of Chemical Analysis," W. H. Freeman and Co., San Francisco, Cal., 1939, p. 334.

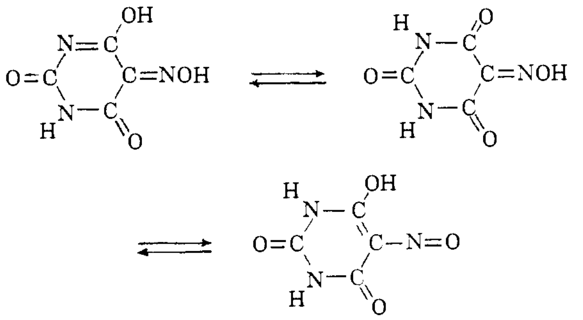

Fig. 1.—Violuric acid equilibrium structures.

Instruments.—Spectral measurements were made with a Beckman Model DU spectrophotometer using 1 cm. matched cells; *p*H measurements with a Photovolt Model 110 *p*H meter, including the titration data obtained for violuric acid; polarographic measurements with a Sargent Model XXI Recording Polarograph.

Spectra and Spectrophotometric Formula Determinations. A. Violuric Acid.—Standard violuric acid solutions were prepared by weighing to the nearest milligram about 0.5 g. of the dried reagent and dissolving in 500 ml. of distilled water. Several separate samples (from different lots) of the Kodak material and a sample of du Pont material were used to determine any possible consequence of impurities. All spectrophotometric measurements were made in a 21° constant temperature room. Continuous variations studies[7] were employed at three different acidities. The wave length of these studies was that of maximum absorbance, 605 mμ for Fe, 410 mμ for Cu, 370 mμ for Co. The metal ions and ligand both had negligible absorbances at the wave lengths used, thus the absorbance of each varying concentration solution was assumed due only to the iron-violurate complex. The chloride as well as the sulfate of Fe(II) was used as its metal salt to check any possible effects of the anion. There were none. The solutions were sufficiently dilute (around 10^{-4} *M*) to minimize chloride or sulfate interference in any case. Nitrates as well as sulfates were the anions with Co and Cu. The solutions were 0.04 *M* in acetate which served as the buffer at the acidities where quantitative studies were made. This ensured constant ionic strength during continuous variation studies. Data are contained in Fig. 2. Approximately 100 times the concentration of metal ion and violuric acid were required for observable color formation with Fe(III) compared to Fe(II), Cu(II) and Co. Both reagents and complex absorbed very strongly at the wave length of maximum absorbance (353 mμ). A continuous variations study was not attempted.

B. 1,3-Dimethylvioluric Acid.—Reactions of Fe(II), Cu(II), Co and Fe(III) with 1,3-dimethylvioluric acid produced species whose visible spectra were identical, within limits of experimental error, to those obtained with violuric acid over the *p*H range 3-7. No increase in spectral intensity for constant metal ion and reagent was obtained beyond *p*H 7. The colored products did not show absorption maxima shifts with *p*H, but spectral intensity at the maxima decreased rapidly beyond *p*H 7 except for Co.

Synthesis of 1,3-Dimethylvioluric Acid. Dimethylbarbituric Acid.—In a 3-liter round-bottomed flask, 35 g. of sodium was allowed to react with 500 ml. of absolute ethanol under reflux. One hundred eighty g. of ethyl malonate and 85 g. of dry dimethylurea (dissolved in 500 ml. of absolute ethanol) were then added and the mixture refluxed for 12 hours. At the completion of the reaction, 800 ml. of hot water and 90 ml. of concd. hydrochloric acid were added with stirring. The mixture was filtered and placed in a refrigerator overnight. White needles of dimethylbarbituric acid were recovered; m.p. 120–123°, yield 25%.

Dimethylvioluric Acid.—The product of the previous reaction (dimethylbarbituric acid) was placed in a 1-liter beaker with 50 ml. of concentrated hydrochloric acid, heated and stirred until dissolved. Twenty g. of sodium nitrite in 10% solution was added with stirring (NO_2 violently evolved) and the mixture cooled. Pale-pink needles in 50–60% yield precipitated and were recrystallized in ethanol; m.p. 139–140°. *Anal.* Calcd. for: C, 38.9; H, 3.78; N, 22.7. Found: C, 38.9; H, 3.9; N, 22.7.

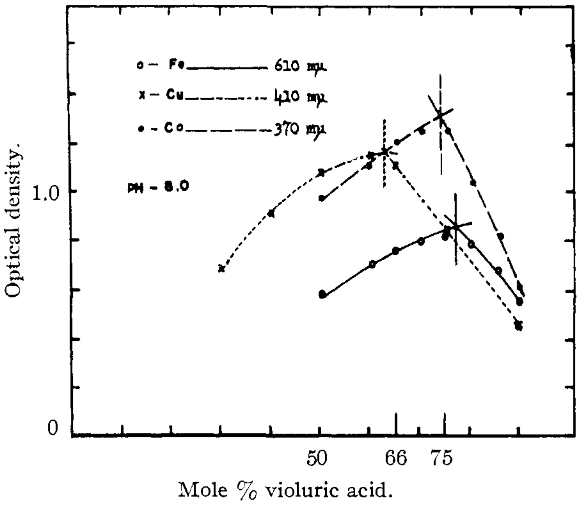

Fig. 2.

Dissociation Constants of 1,3-Dimethylviolurate Chelates of Cu(II) and Fe(II).—The method of Edmonds and Birnbaum,[8] was used to obtain dissociation constants. This method utilizes a large excess of the ligand in two or more different concentrations with constant amount of metal ion. For a reaction of the type

$$Fe^{++} + 3(C_6H_6N_3O_4)^- = Fe(C_6H_6N_3O_4)_3^-$$

$$K_{\text{dissoc}} \cong \frac{b^3d^3\,(E_y - E_x)}{d^3E_x - b^3E_y}$$

where *b* and *d* are the stoichiometric concentrations of ligand in the solutions and E_x and E_y the respective absorbances of the resulting chelate. The metal ion concentration does not appear in the expression. The constants for Fe(II) and Cu(II) were obtained at *p*H 6.5 where it is assumed all of the dimethylvioluric acid is in the ionic form. The data from these measurements are in Table I.

TABLE I

Ionic strength, 0.04 (determined by the acetate buffer concn.).

Cu(II) ($5 \times 10^{-5}M$)		Fe(II) ($5 \times 10^{-5}M$)	
M (ligand)	*E*	*M* (ligand)	*E*
4.62×10^{-4}	0.079	4.62×10^{-4}	0.331
9.24×10^{-4}	.112	9.24×10^{-4}	.512
1.37×10^{-3}	.115	1.37×10^{-3}	.558
$k = 1.1 \times 10^{-7} \pm 0.2 \times 10^{-7}$		$k = 7 \times 10^{-11} \pm 4 \times 10^{-11}$	

Evidence for the Existence of Co(III) Violurate.—Spectrophotometric Rate Studies.—The rate of color development of the colored cobalt species was measured in a solution of 0.5% sodium hypochlorite, and in a 1% solution of hydroxylamine, both solutions buffered at *p*H 7.9. Color formation was practically instantaneous in the first case, quite slow in the second. A more careful study at *p*H 6.3 was carried out comparing the formation rates of the species in the presence of 2% sodium sulfite, 0.5% hydrogen peroxide and no added agent. The solutions were identical in cobalt and violuric acid content. Measurements were made at 370 mμ.

Polarographic Studies.—All samples were treated identically. Polarograms were taken in 1.0 *M* KCl supporting electrolyte at 25°. Oxygen was removed by flushing the system with nitrogen for 15 minutes. A maximum suppressor was not used after it was discovered no alteration occurred in the polarograms with or without the addition of gelatin. Good residual curves were obtained. Two representative polarograms of violuric acid and acetate buffer with and without the added cobalt are shown in Figs. 3 and

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[7] A. Job, *Ann. Chim.*, **9**, 113 (1920).

[8] S. M. Edmonds and N. Birnbaum, THIS JOURNAL, **63**, 1471 (1941).

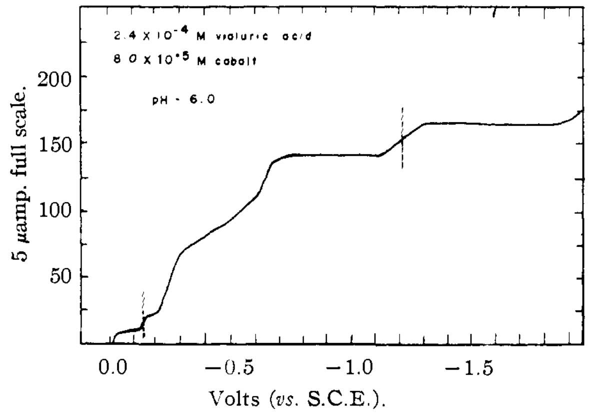

Fig. 3.

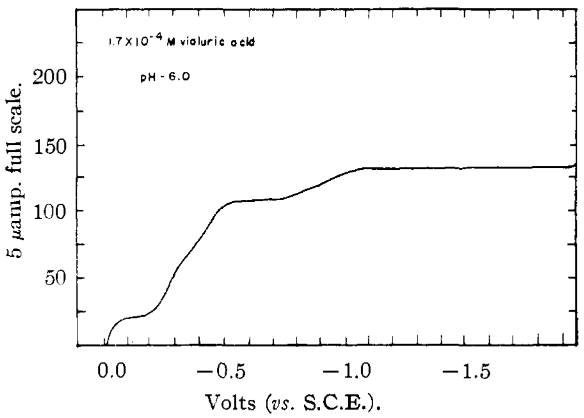

Fig. 4.

4. The chelate was allowed to develop without the addition of oxidants.

pH Titration of Violuric Acid and Dimethylvioluric Acid.—Fifty-ml. aliquots of 0.00870 *M* violuric acid and 0.005 *M* dimethylvioluric acid were titrated with 0.0204 *N* sodium hydroxide. The solutions were magnetically stirred and the *p*H was determined after small volume increments. The loss of more than one proton for either compound is not indicated below *p*H 10–11 by the data. Titration data indicate *pK* values for these compounds are equal.

Results and Discussion

The formation of violurate complexes of Fe(II), Cu(II) and Co that occur in the ratio 3:1, 2:1, 3:1 suggest that violuric acid and 1,3-dimethylvioluric acid are bidentate ligands. This would be consistent with the common coördination numbers of the metal ions involved. Continuous variations studies indicate no change in metal ion–ligand ratio over the *p*H range 4–8. The shift of absorption maxima is about 10 mμ to shorter wave lengths in all cases, excepting Co. The metal ion–ligand ratio could remain the same with initial displacement and coördination by hydroxyl at high *p*H but this would probably produce more marked spectral variations.

The chelating ligand is indicated to be a univalent anion. Titration of violuric acid with sodium hydroxide shows only one break and indicates that this reagent exists as a univalent anion in aqueous solution below *p*H 9 and probably, though not necessarily, below *p*H 11.

The chelates formed would have these formulas

$Fe(C_4H_2N_3O_4)_3^{\ominus}$, $Fe(C_4H_2N_3O_4)_3$, $Cu(C_4H_2N_3O_4)_2$
$Co(C_4H_2N_3O_4)_3$.

A previous study of the iron system by Kuster[3] indicated a 2 to 1 ratio of reagent to Fe(II). This formulation was based on the recovery of an insoluble product from ether with subsequent analysis. From the amounts of reagent and metal ion used it seems clear that the salt recovered was ferrous ferroviolurate, $Fe(Fe(C_6H_6N_3O_4)_3)_2$, in which the reagent–metal ion ratio is indeed 2 to 1.

Violuric acid previously has been indicated to exist as keto–enol tautomers. The compound 1,3-dimethylvioluric acid should eliminate the keto–enol equilibria involving the ring nitrogens and reduce the tautomeric complexity of the system. This compound previously has been prepared *via* a degradation of caffein.[9] Although reactions of nitrous acid with β-keto esters are well known and the analogy here is clear, to our knowledge our synthesis of dimethylvioluric acid has not been reported.

Increasing *p*H produced an increasing absorbance even to *p*H 10 with the metal ion species cited previously with violuric acid. This does not occur with 1,3-dimethylvioluric acid. Methyl substitution on the 1,3-ring positions blocks keto–enol equilibria involving the ring nitrogens. If the reacting species were dinegative, the removal of the second proton with increasing *p*H would follow logically. All evidence gathered, however, indicates the reacting species to be uninegative under the conditions employed. A rigorous explanation of this effect has not yet been possible.

The cobalt chelates with violuric acid and 1,3-dimethylvioluric acid are the most stable of the chelates investigated. This was indicated by preferential removal of metal ion from solution, invariably occurring Co replacing Cu replacing Fe in the chelate. In plots of absorbance *vs.* the ratio moles reagent/moles metal ion, only chelates that are very stable yield plateaus. Fe(II) and Cu(II) curves continue to rise indicating a large degree of dissociation. Only Co shows a plateau.

The fact that formation of the Co chelate was very rapid in the presence of oxidants and very slow in the presence of reductants led to a polarographic examination of the system. Polarographic evidence concerning the Co species is contained in Figs. 3 and 4. Figure 4 indicates the polarographic reduction curve obtained for violuric acid. A thorough study of this curve has not been made but it would appear that multiple reductions are taking place. Figure 3 indicates the polarogram obtained with the Co species. A considerable alteration of the reduction waves of the reagent was observed. Two new, sharply defined reduction waves appeared, as contrasted with the reduction waves of the reagent, at −0.14 and −1.21 v. The wave at −0.14 v. was exactly one-half the height of the wave at −1.21 v. It has been noted that the second wave, at −1.21 v., corresponds to a reduction potential value for Co(II) cited by Kolthoff and Lingane[10] under identical solution conditions of −1.20 v. These facts are suggestive, when considered with the preceding information, of reduction waves of Co(III) and Co(II). They further

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[9] H. Biltz and T. Hamburger, *Ber.*, **49**, 649 (1916).

[10] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publ., New York, N. Y., 1946, p. 284.

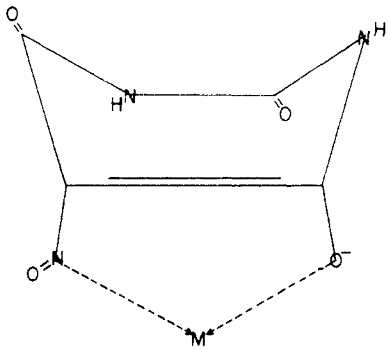
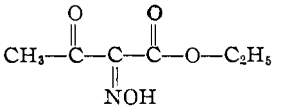


Fig. 5.

suggest that Co(II) does not react at all with this reagent. The reduction polarogram of violuric acid is complex and may not be open to such simple interpretation. However, the appearance of a new wave corresponding to that of normal Co(II) salts and the reproducibility of the wave at −0.14 v. makes the foregoing interpretation less doubtful. In cases of known Co(II) chelates and complexes the reduction potential invariably is decreased on chelation or complexation. Since no decrease is observed, Co(II) is likely not chelated by violuric acid. It is known that a larger number of Co(III) chelates and complexes are more stable than the corresponding Co(II) chelates and complexes. This fact, supported by polarographic and spectrophotometric rate study data suggest strongly the presence of Co(III).

The oxime of ethyl acetoacetate has a structure similar to violuric acid in that the oxime carbon is flanked by carbonyl groups.



$$CH_3-\overset{O}{\overset{\|}{C}}-\underset{NOH}{\underset{\|}{C}}-\overset{O}{\overset{\|}{C}}-O-C_2H_5$$

The authors prepared this compound by the method of Jovitschitsch.[11] It dissolved somewhat sparingly in water and its solutions gave colored products with Fe(II), Cu(II) and Co at *p*H 6 that were visually identical with those obtained using violuric acid and 1,3-dimethylvioluric acid. The Co reaction was again slow but was practically instantaneous upon the addition of hydrogen peroxide. Comparison of the spectra of the violurate and ethyl acetoacetate oxime chelates showed a striking similarity.

From the data previously cited, a reasonable formulation of the structures of the metal ion violurates seems possible. Evidence at hand can be summarized as follows: (1) violurate and 1,3-dimethylviolurate exist wholly as uninegative anions above *p*H 6. (2) There is no evidence to indicate a dinegative violurate anion below *p*H 9. (3) Cobalt violurate and cobalt 1,3-dimethylviolurate complexes have identical visual and ultraviolet spectra. (4) The ultraviolet spectrum of cobalt ethyl acetoacetate oximate is very similar to that of Co violurate except that the absorption maximum occurs 20 mμ lower in the ultraviolet.

Data 1–2 indicate the chelating ligand reacts as a uninegative anion; 3 indicates that the effect of tautomerism involving the ring nitrogens is at most minimal; 4 indicates the grouping -CO-C(NOH)-CO- is probably the reacting group of both ligands since it is the only bidentate functional grouping common to both molecules. The structure drawn in Fig. 5 represents the most likely chelate product of univalent violurate anion on the basis of this evidence. The boat form of the chelating agent is necessary if the atoms chelating the metal ion are to lie in the same plane. The nitroso form of the oximate is indicated because keto carbonyls are rarely involved in coördination.

Spectrophotometric Determination of Copper with Violuric Acid.—The copper violurate chelate, which is stable over the *p*H range 2.5–10.0 and which exhibits an absorption maxima at 410 mμ can be utilized for the determination of copper. The procedure developed was relatively simple and fast, gave analyses of less than 3% error and was applied successfully to samples of widely variant Cu percentage. The chelate obeys Beer's law over the range 1–15 p.p.m. Cu.

TABLE II

INTERFERENCES

Cations		Anions	
Species	Tolerance	Species	Tolerance
Co	None	Cyanide	None
Fe(II)	Fe=Cu	Citrate	100 p.p.m.
Cd(II)	1000 p.p.m.	Tartrate	100
Zn(II)	250	Phosphate	1000
Sn(II)	30	Sulfate	1000
Nd(II)	200	Nitrate	1000
Al(III)	1000	Chloride	1000
		Acetate	1000

TABLE III

ANALYSES OF Cu-BEARING SAMPLES

		Theory, %	Found, %	Error, %
1	Copper ore	5.97	5.95	−0.34
			6.02	0.84
2	Copper ore	9.67	9.35	−3.3
			9.95	2.9
3	Monel metal	30.00	30.0	...
			29.8	−0.67
4	NBS Al–Cu alloy number 85b	3.99	3.86	−3.2

Procedure.—Weigh approximately half-gram samples of the Cu bearing material and transfer to a suitable container. Add 25 ml. of 6 *M* nitric acid and heat, if necessary, to dissolve. Cool and neutralize with sodium hydroxide. Reacidify by adding 1 ml. of 6 *M* acetic acid. Transfer to a 500-ml. volumetric flask and dilute to the mark. Take an aliquot which will fall in the range, 1–15 p.p.m. Cu. Transfer the aliquot to a 100-ml. volumetric flask, add 10 ml. of 0.010 *M* violuric acid and 2 ml. of acetate buffer (*p*H 5.8, approximately 2.5 *M* in sodium acetate, 0.25 *M* in acetic acid). Measure the absorbance with a suitable spectrophotometer at 410 mμ and compare with a standard curve prepared by the same procedure, from electrolytic Cu. Interferences and results of analyses are given

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[11] M. Jovitschitsch, *Ber.*, **28**, 2685 (1895).

in Tables II and III. The precipitate of aluminum hydroxide obtained in III-4 on neutralization, reacidification and dilution to volume, was allowed to settle and an aliquot withdrawn from the supernatant. This procedure was found more satisfactory than to attempt to separate the aluminum by filtration.

MIDDLETOWN, CONN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY]

Kinetic Studies of the Thionine–Iron System. I

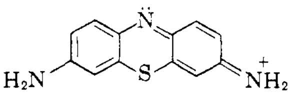
BY R. HARDWICK

RECEIVED FEBRUARY 17, 1958

The kinetics of the photosensitive reaction thionine + ferrous ion = semithionine + ferric ion and of the second reduction step, semithionine + ferrous ion = leucothionine + ferric ion, is investigated. Conclusions made from photostationary state data are checked against initial rate data and reverse rate data with fair agreement. The rate constant for the reverse (color restoring reaction) is evaluated and the ratios of other constants are given. The long lived active thionine species produced by light absorption is reduced by ferrous ion. Most of the reduced dye seems to be present as the free radical semithionine, which reacts with ferric ions to produce again the unexcited purple thionine. Certain quantum yield results are explained on the basis of quenching by ferric ion. A reaction mechanism is proposed.

Introduction

Thionine (thio) is a purple dye of the thiazine class, probably having the structure



The dye can be reversibly reduced[1] to give two colorless species, the free-radical semithionine (semi) or the doubly reduced leuco form (leuco).

In aqueous solutions, one or more protons may be added by the dye and by its reduced form depending on the *p*H. The oxidation reduction potential of the system thio–leuco has been found[2] to be a linear function of *p*H in the range 1 to 4. The standard electrode potentials may be estimated for the two oxidation steps, leuco = semi + e^- and semi = thio + e^-, to be about -0.53 and -0.39 v., respectively, at *p*H 1. (The estimation is made for *p*H 1 because the present experiments were carried out at that concentration.) The electrode potential for the reaction ferrous = ferric + e^- is -0.77 v. Accordingly, the two equilibria

$$\text{leuco} + \text{ferric} = \text{semi} + \text{ferrous}$$
$$\text{semi} + \text{ferric} = \text{thio} + \text{ferrous}$$

lie entirely to the right (*i.e.*, ferric ions are much stronger oxidizing agents than either thio or semi). The equilibrium constant, [semi][ferrous]/[leuco][ferric], would be about 10^4 given these estimated electrode potentials (*cf.* sec. c, Results). Determination of the potentials for the two single steps depends on use of the disproportionation constant and an estimation of the concentrations of semi and leuco in a half titrated solution at equilibrium. Since these concentrations cannot be conveniently measured, the E_0 values are approximate.

Thio molecules which have been excited by absorption in the band having a peak at about 5990 Å. are more easily reduced than unexcited molecules. This phenomenon may be demonstrated by exposing a solution of thio and ferrous ion to sodium vapor radiation (or for that matter, to sunlight). The equilibrium between thio and its reduced forms is shifted to the extent that the purple solution loses nearly all its color. The rate of bleaching depends upon light intensity and the various concentrations, but under typical conditions the bleaching process takes five or ten seconds. As long as irradiation continues, the solution remains in this "photo-stationary" bleached state. When the light is removed, the equilibrium is restored to its former position within a few seconds, and the solution again becomes purple. In oxygen free solutions, the process may be repeated again and again, although the effect gradually weakens. Figure 1 is a plot of the light transmitted by such a solution against time with shutter actions noted.

A more complete preliminary discussion is given by Rabinowitch[3] who made the first detailed photochemical investigation of the thio–iron system. The mechanism of the reaction was studied by determining the dependence of the position of the photostationary state on the concentration of the reactants and on the light intensity. Relations were given for these variables, but no rate study was attempted. A second paper by Rabinowitch[4] discussed the photogalvanic properties of the system, a subject of considerable interest to workers in the solar energy conversion field. Michaelis and co-workers[1] and Clark and co-workers discuss the system from a non-photochemical point of view.

There have been several studies of the kinetics of the reaction between thio and organic reducing agents in non-reversible systems.[5] Pestemer, in a rate study with thio and thiosinamine, showed that the initial step of the reaction is the transfer of an electron rather than a hydrogen atom. Pestemer also has discussed the role of long-lived excited states, presumably triplets, in the reaction, a subject which recently has received further attention from Oster and co-workers.[6] In some of

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(1) W. M. Clark, B. Cohen and H. D. Gibbs, *Public Health Reports*, **40**, 1131 (1925); W. M. Clark, "The Harvey Lectures," 1933, pp. 67–115; L. Michaelis, S. Granick and M. P. Schubert, THIS JOURNAL, **62**, 204 (1940); **63**, 351 (1941).

(2) W. M. Clark, *Cold Springs Harbor Symposia*, **VII**, 1 (1939).

(3) E. Rabinowitch, *J. Chem. Phys.*, **8**, 551 (1940).

(4) E. Rabinowitch, *ibid.*, **8**, 560 (1940).

(5) M. Pestemer, *Z. Elektrochem.*, **58**, 121 (1954); E. Matijevic, *Arhiv. Za. Kem.*, [XXI] **1**, (1949); E. Matijevic and K. Weber, *Rec. trav. chim.*, **70**, 481 (1951).

(6) G. Oster and A. H. Adelman, THIS JOURNAL, **78**, 913 (1956).