THIOUREA AS ADDITION AGENT IN COPPER ELECTRODEPOSITION

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by

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ABSTRACT

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Thiourea in acid copper sulfate solution formed a sulfur-coordinated charge transfer complex with cupric ion

$$\lambda_{max} = 340\ \mathrm{nm}, \varepsilon_{340} = 3300\ \mathrm{M^{-1}cm^{-1}}$$

(stability constant = 2.2 ± 0.2 at 25°C). Cuprous thiourea complexes and formamidinedisulfide were formed as a result of electron transfer from sulfur to cupric ion. The disulfide decomposed slowly in acid solution by nucleophilic attack of hydroxide ion at the disulfide bond. The hydrolysis of formamidine-disulfide and of di-(tetramethylformamidine) disulfide at $pH < 4$ obeyed second order kinetics with rate = k[disulfide][hydroxide]. Activation parameters were

$$\Delta E^{\ddagger} = 7.8\ \mathrm{kcal\ mole^{-1}},\ \Delta S^{\ddagger} = -2\ \mathrm{e.u.}$$

for formamidinedisulfide and

$$\Delta E^{\ddagger} = 1.8\ \mathrm{kcal\ mole^{-1}},\ \Delta S^{\ddagger} = +16\ \mathrm{e.u.}$$

for di-(tetramethylformamidine)disulfide. Cleavage of the disulfide bond in the transition complex is proposed as the rate-determining step. Formamidinedisulfide and uncomplexed thiourea were not active as addition agents.

Complexes of thiourea with copper were cathodically reduced to copper sulfide which appeared to be responsible for levelling of the deposit, probably by preferred reduction of complex at micro-peaks on the electrode surface. A small sulfur content (> 0.01 wt % S) in the deposit is necessary for levelling to occur, and blocking theory is not applicable to explain the observed high overpotentials in the presence of thiourea. Decrease in levelling powers of the bath with time after adding thiourea is attributed to the agglomeration of monomolecular cuprous-thiourea ions to form aggregates of insoluble thiourea complex with cuprous sulfate.

RESUME

Département de Chimie Hans-Ulrich Heintze Ph.D.

LA THIOUREE COMME ADDITIF DANS LA DEPOSITION DU CUIVRE

RESUME

En solution acide de sulfate de cuivre la thiourée forme un complexe cuivrique coordoné par le soufre

$$\lambda_{max} = 340 \text{ nm}, \varepsilon_{340} = 3300 \text{ M}^{-1}\text{cm}^{-1}$$

(constante de formation = 2.2 ± 0.2 à 25°C). Les complexes cuivreux de la thiourée et de la dithiodiformamidine se produisent après le transfer d'un éléctron du soufre vers l'ion cuivrique. En solution acide la dithioformamidine est decomposée lentement par l'attaque nucleophile sur le lien -S-S-. La cinétique de l'hydrolyse de la dithiodiformamidine et de la dithiodi-(tetramethyl)-formamidine est du second order, à pH < 4; la vitesse de réaction = [dithioformamidine][hydroxide]. Les paramètres d'activation sont

$$\Delta E^{\ddagger} = 7.8 \text{ kcal mole}^{-1}, \ \Delta S^{\ddagger} = -2 \text{ e.u.}$$

pour la dithiodiformamidine et

$$\Delta E^{\ddagger} = 1.8 \text{ kcal mole}^{-1}, \ \Delta S^{\ddagger} = +16 \text{e.u.}$$

pour la dithiodi-(tetramethyl)-formamidine. La rupture du lien -S-S- est proposée comme étape déterminante de l'hydrolyse. La dithiodiformamidine et la thiourée non complexée sont inactifs en tant qu'additifs.

Les complexes de la thiourée avec le cuivre sont reduits à la cathode en sulfure de cuivre, lequel apparait être responsable de l'uniformité du dépôt, probablement par la reduction préferentielle du complexe aux pics de la surface de l'éléctrode. Une faible quantité de soufre (> 0.01 % en poids) dans le dépot est nécessaire pour que le nivellement se produise. La diminution avec le temps de la capacité de nivellement du bain après addition de thiourée est attribuée à l'agglomeration des ions monomoléculaires cuivre (I)-thiourée, ceux-ci formant dès agregats insolubles de complexes de la thiourée avec le sulfate cuivreux.

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PREFACE

PREFACE

The research reported in this thesis has involved some studies of a distinctly chemical aspect and others largely of an electrochemical type. As a consequence, it seemed desirable to present the results of the study in the form of separate sections, for each of which an attempt has been made to include an appropriate introduction, together with the data relevant to that particular study and discussion of these results. To place the overall investigation in proper perspective, some general introductory remarks precede the presentation of the more specialized chemical and electrochemical studies. The presentation is concluded with some brief general comments that seek to coordinate the results of the individual studies, and indicate the relative importance of these to the elucidation of the function of thiourea as a brightening and levelling agent in electrodeposition from acid copper sulfate solutions.

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THIOUREA AS ADDITION AGENT IN COPPER ELECTRODEPOSITION

GENERAL INTRODUCTION

The electrodeposition of metals has long been a commercially important process in its applications to electrorefining, electroforming and electroplating. Modern society relies heavily on electrochemical coatings and deposits of nickel, copper, chromium, silver, gold and many other metals. Nickel and copper, the most important of the commercial plating systems, have been the most intensively studied, and a wealth of empirical data is available.

Electrolysis occurs in a bath which occasionally consists of a fused salt or an organic electrolyte, but in commercial practice, it is almost invariably an aqueous solution. The metal to be electroplated must be present in the plating bath in a concentration high enough to permit passage of large currents, and a high solubility is the first of several requirements that limit the number of useful plating systems for copper. In addition to being very soluble, the salt must be reasonably inexpensive, stable in the plating bath and preferably not highly corrosive. There are other, and more subtle, limitations on the choice of salt that may be used in electrodeposition. For example, acid cupric chloride has desirable characteristics in respect of all of the above criteria, but it cannot be used since the formation of insoluble films of cuprous chloride at both anode and cathode makes practical copper electrodeposition virtually impossible. Again, cupric nitrate is very soluble, but the reduction of nitrate ion at a potential of + 0.7 volts (measured against a standard hydrogen electrode, SHE) leads to a low current efficiency for copper deposition at high current densities. Acid cupric perchlorate has many properties to commend it as an electrolyte, but is costly and presents an explosion hazard.

Acid copper sulfate satisfies all the requirements for a good electrodeposition bath, and was the only acid copper plating solution of commercial importance until the use of fluoborate solutions was introduced after 1940.*

The acid copper sulfate bath has a high conductivity and low electrode polarization, so that only low voltages are required for electroplating. Anode and cathode current efficiencies are both approximately 100%, as a consequence of which only slow changes occur in the composition of the solution with prolonged use.

Finally, the system is not readily affected by ionic impurities. Good deposits may be obtained from solutions

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* Not mentioned here, but of importance for many plating applications are the alkaline baths such as copper cyanide, which have been extensively surveyed elsewhere. (1)

that contain relatively large quantities of nickel, cobalt, zinc and iron because conditions are not favourable for co-deposition of these metallic impurities with copper. For example, less than 2 ppm nickel was co-deposited with copper in a sulfate bath that contained 15 g/ℓ nickel (2).

The acid copper sulfate bath does have drawbacks, however, since it tends to encourage coarse, nodular deposits and frequently the spontaneous formation of "whiskers" (3) which, in present day copper refineries, are likely to cause short-circuits. The relatively poor surface qualities of electrodeposits from acid copper sulfate baths required substantial costs for buffing and polishing the electroplated parts to the desired finish. This led to a search for modifications to the plating bath, and thereby the electrodeposition process, to enable the production of smooth and bright coatings that would require minimum, or no subsequent attention.

This search began virtually with the commencement of commercial electroplating early in the nineteenth century, and the developments rested, for many years, on careful, but relatively unsystematic observations.

Some insight may be gained into the approach used by early electroplaters from an account given by N.S. Keith, in the discussion section of the first symposium on the electrodeposition of metals held by the American Electrochemical Society and published in their Transactions in 1913 (p.294).

> While visiting a nickel-plating establishment early in the 1870's, Keith had noticed that one of the platers was in the habit of chewing tobacco and expectorating the tobacco juice into the plating solution. When asked why he did this, the plater simply replied that it had been found to give good results. Similarly, it had been observed that storing nickel solutions in wooden barrels sized with glue gave good nickel deposits (4), and this eventually led to the use of glue, and later gelatine, as an addition agent.

Gelatine, glue and molasses were among the addition agents used prior to 1913 to suppress formation of large crystals and whiskers in deposition from acid copper sulfate and even at this early date, it was thought that some form of adsorption of the addition agent onto the electrode must be involved (5).

Taft (4) summarized the theories of addition agent behaviour in 1933 and succeeded in demonstrating that gelatine or its decomposition products were occluded in copper from baths containing high gelatine concentrations. It was acknowledged, however, that science was far from being able to account for the behaviour of numerous addition agents which platers had used over the years.

In a review on acid copper electroplating and electroforming, J.H. Winkler (6), discussed available levelling agents and anticipated the development of a brightener for deposition from acid copper sulfate similar to those which had already been developed for nickel plating from a Watts bath.

At that time, the American automobile industry was sponsoring a screening program for copper brighteners. The search had been prompted by the shortage of nickel as undercoating for decorative chrome plate, which prohibited the use of a relatively thick deposit of bright nickel to level a rough copper undercoating. In 1942,Clifton and Phillips (7) published an account of the first acid copper sulfate bath for the deposition of bright copper, which contained thiourea as brightener and molasses as a secondary addition agent to reduce striations in areas of low current density. The smooth and bright deposits that were obtained did not require buffing and polishing prior to nickel plating. However, the bath gave unsatisfactory deposits after prolonged operation, even with the addition of more thiourea and molasses, and it then had to be purified by filtration. This behaviour was thought to be due to an accumulation of an hydrolysis product of the thiourea, and was not further investigated. No method could be devised to monitor the thiourea concentration analytically, and good plating characteristics were the only criterion by which its presence in sufficient amount was recognized.

Thirty years later, thiourea is still being used extensively as a levelling agent in copper refining and as a brightener not only for copper, but also for nickel (8-13), cobalt (14,15) and iron (16). Surprisingly, however, relatively little progress has been made in gaining an understanding of how and why thiourea and other addition agents modify electrodeposited metals.

The lack of understanding of the effects of addition agents may be explained partly by the complexity of the systems. No completely satisfactory model has yet been proposed to explain even electrocrystallization from highly purified electrolytes onto single crystals of the same metal.* At present, electrochemical theory and practice have reached a very high degree of sophistication in applications employing polarized liquid electrodes and systems where only species in solution are involved, with no change in the surface of the electrode (17). At solid electrodes, however, the simple case of adsorption of ions or organic molecules presents difficulties due to surface contamination and non-reproducibility, even for polished single crystals in the absence of current flow. In addition, there is a lack of experimental methods for obtaining information on adsorption at solid electrodes. Changes in surface tension due to adsorption at interfaces between liquid metals and solutions are well

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* Models to account for electrocrystallization of metals may be found in textbooks such as those by Raub and Müller (18), Bockris and Razumney (19), and several others (e.g. 20,21).

documented, and represent the oldest method of obtaining detailed information on surface coverage of electrodes of mercury and gallium at temperatures above their melting points. For solid metals, the method is obviously not applicable, and more indirect methods must be employed.

The oldest and most frequently used technique for studying addition agents is based on the often drastic increase in electrode polarization caused by the presence of trace levels (10^{-6} to 10^{-2} M) of organic compounds in the electrolyte. The increased overpotential in the presence of additive is usually explained by the site-blocking theory, according to which adsorption of the additive onto the metal surface reduces the surface area available for electrodeposition with a concomitant increase in true current density and a correspondingly higher overpotential. The overpotential increase depends on the concentration of addition agent in solution, and the main use of overpotential data has been to determine the concentration of additive in an electrolyte (e.g. 22). The fact that some additives lower the electrode polarization (e.g. nitrate ion) obviously cannot be explained by this model unless an increase in true surface area were proposed. However, copper deposited in the presence of nitrate ion appears quite smooth, so that this proposal would seem to be untenable.

Some workers have sought to obtain information about the adsorbed species by applying the simple site-blocking theory (23) and the assumption that adsorption and desorption of additives on the metal are so rapid that no adsorbed molecules are trapped by the growing deposit (24). On the basis of these assumptions, overpotential increases in the presence of additive molecules have been subjected to a Bockris-Swinkels adsorption model*, apparently to derive free energies of adsorption and surface interaction parameters for molecules on the surface during copper electrodeposition (25-27).

The formation of complexes between the additive and other constituents of the electrolyte has been postulated to explain the high polarization in the presence of addition agents (22,28). Films of insoluble complex in the diffusion layer are said to hinder the deposition process and periodic precipitation of these films onto the cathode in a Liesegang-type phenomenon has been claimed to account for the laminar structure of many bright deposits of copper and nickel. It has been shown that benzotriazole, which causes laminar deposits to be formed from acid copper sulfate solutions, forms insoluble polymeric complexes with cuprous ions and that significant amounts (0.001 to 0.5 wt %) of this additive are occluded in the deposit (22).

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* The applicability of this model to adsorption with simultaneous electrocrystallization will be discussed later.

Determination of the amount of additive in both the solution and in the deposit has always presented a problem because of the small quantities involved. Early investigators deposited copper from two identical cells placed in series. One cell was filled with pure electrolyte and the other contained the same electrolyte with addition agent present. When the deposit obtained in the presence of additive was heavier than that from pure electrolyte, the "excess deposit weight" was attributed to occluded additive (e.g. 29). With gelatine as additive, combustion analysis for carbon, nitrogen and sulfur in the deposit was used to confirm the presence of organic matter.

The use of addition agents labelled with radioactive isotopes has found widespread use in studying the occlusion of addition agents. By labelling several parts of the additive molecule (e.g. with $^{35}S, ^{14}C, ^{3}H$), it is possible to detect whether the molecule is trapped as an entity or as fragments formed at some stage prior to incorporation. With thiourea*, such measurements have shown that mainly sulfur is occluded in the deposit, with varying, much smaller amounts of carbon (30,31). Some workers have interpreted

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* In these general introductory comments, it seems useful and relevant to illustrate several general aspects of studies made with addition agents by reference to results that have been obtained with thiourea. More extensive discussion of some of these will be necessary subsequently in discussing the data obtained during the present investigation.

this as direct electrochemical reduction of thiourea to give sulfide ions, which then precipitate as copper sulfide (32-34). Others (35) have thought that cleavage of the thiourea occurred by an hydrolysis step. Desulfuration by dissolved oxygen of thiourea adsorbed onto the copper cathode has also been proposed (30).

Long before the use of thiourea as an addition agent, it had been demonstrated that thiourea is oxidized to formamidiniumdisulfide by cupric ion, with concurrent formation of cuprous-thiourea complexes. Nevertheless, studies of thiourea as a brightener in deposition from acid copper sulfate largely neglected complex formation and reactions of thiourea with the electrolyte. The possibility that it might be oxidized by cupric ion was mentioned in some reports (36-39), but the possible effects of such a reaction on levelling and brightening powers of the bath were not considered.

Formation of cuprous-thiourea complexes was thought to be of importance by Shreier and Smith (28), but was not considered further until Javet and Hintermann(40) attributed an UV absorption maximum at 340 nm to a cuprous-thiourea species in the acid copper sulfate bath. A complex chemical system is indicated by the isolation of elemental sulfur (41), ammonium ion and urea (42) from acid copper sulfate solution to which thiourea had been added, but no detailed explanation was offered for these observations.

Investigations of open-circuit adsorption of thiourea on copper have been made in organic solvent systems and in dilute aqueous solution using thiourea labelled with the radioactive isotopes ^{35}S and ^{14}C. Trivich et al (43,44) interpreted their results with ^{35}S labelled thiourea in terms of adsorption of the whole molecule, whereas Llopis et al (45-47), using thiourea that contained either ^{35}S or ^{14}C, demonstrated that the radioactivity stemmed from films of copper sulfide, with only traces of carbon present. Their results were interpreted in terms of oxidative desulfuration by dissolved oxygen, since the formation of sulfide occurred only in the presence of oxygen. However, it is known that in acid solution (e.g. 0.01 N HCl) thiourea will cause corrosion of copper with formation of cuprous thiourea complexes. If it may be assumed that this process can also take place in neutral solution, then formation of cuprous thiourea complex could be the first reaction (cuprous ions being formed by reaction of copper with dissolved oxygen), followed by alkaline hydrolysis of the complex to form sulfide.

The distribution of additives in electrodeposited metals has been studied mainly for nickel, but thiourea is degraded and occluded as sulfide in this case also (8,9,11-13) (similar degradation occurs in deposition of cobalt (14,15) and iron (16). When deposition occurred onto a rough nickel substrate from a Watts bath containing thiourea or other levelling agents, proportionately more metal was deposited on the depressions in the surface than on protrusions (48). By autoradiography and by direct counting, it was demonstrated that the deposit on protrusions contained a higher content of the additive than the metal deposited in the recesses (10,49,50). A similar study of thiourea in deposition from acid copper sulfate solution has confirmed this behaviour (51).

The results were originally interpreted in terms of preferred adsorption on the peaks (10,49,50), but it was later considered possible that a thinner diffusion layer over protrusions permitted a higher rate of adsorption on these areas than in the recesses with a relatively thicker diffusion layer (48).

In general, the practical aspects and common use of thiourea as a levelling and brightening agent continue to make it important as addition agent in electrodeposition from acid copper sulfate solutions, even though its action is not understood. This lack of understanding is due ,in part, to the limited extent to which it has received attention, and ,in part, to contradictions and possible misinterpretations in some or many of the studies that have been made. As a result, no satisfactory model has been proposed to account for the effects of thiourea on the deposition process.

In view of this situation, it appeared interesting and important to investigate further, and in some detail, the oxidation of thiourea and its formation of complexes with copper in acid copper sulfate electrolyte, and to study the electrochemical behaviour of thiourea during copper electrodeposition, with a view to obtaining a better appreciation of the mechanism responsible for its desirable characteristics as an addition agent.

HYDROLYSIS OF FORMAMIDINEDISULFIDE

INTRODUCTION

The time dependence of the addition agent properties of thiourea in acid copper sulfate solutions has been well documented (36-44). The formation of elemental sulfur has also been observed (41), while other studies (52,53) have indicated that the oxidation of thiourea by acid copper sulfate yields the sulfate of formamidiniumdisulfide as the anhydrous salt, $(H_4N_2CS-)_2SO_4$*.

The decomposition of formamidiniumdisulfide ion in aqueous solution was reported in early studies (56,57) to conform to the stoichiometry

$$(H_4N_2CS-)_2^{2+} \rightarrow H_4N_2CS + S + NCNH_2 + 2H^+ \qquad (1)$$

The yields of acid and thiourea were in reasonable accord with this scheme, but that of sulfur was almost 40% less than expected. From the amount of titratable acid liberated during the decomposition of the disulfide, Toennies (58) proposed that it occurred by the sequence

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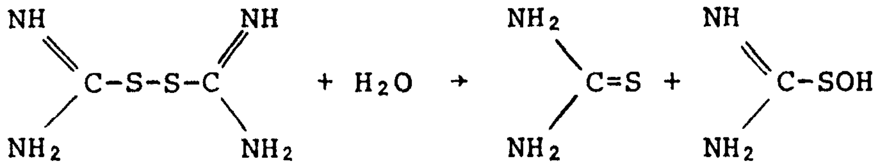
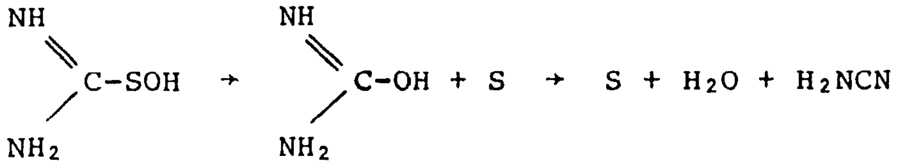
* Salts of formamidinedisulfide were prepared as early as 1875 by Claus (54) but it remained for Storch (55) to establish the disulfide structure for which he proposed the name formamidinedisulfide.



$$\mathrm{HN{=}C(NH_2){-}S{-}S{-}C(NH_2){=}NH} + H_2O \rightarrow \mathrm{(NH_2)_2C{=}S} + \mathrm{HN{=}C(NH_2){-}SOH} \qquad (2)$$



$$\mathrm{HN{=}C(NH_2){-}SOH} \rightarrow \mathrm{HN{=}C(NH_2){-}OH} + S \rightarrow S + H_2O + H_2NCN \qquad (3)$$

Decomposition of the sulfenic acid was assumed to occur spontaneously.

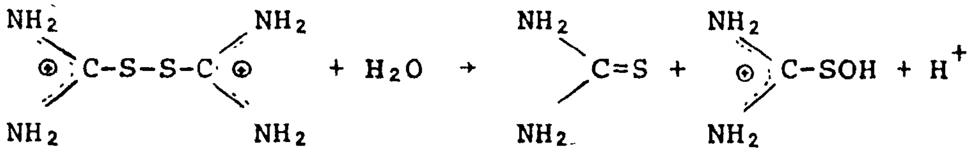
Although this proposal seems to be generally accepted, several objections to it may be suggested:

(i) The amidinium ion $H_2N\overset{\overset{X}{C}}{+}NH_2$, is an extremely weak acid. Its large resonance energy makes the amidine group strongly basic, with relative insensitivity to the nature of a substituent on the carbon atom. The pK_a values for $-NH_2$, $-CH_3$, $-OCH_3$ and $-SCH_3$ as substituents, have been found to be 13.71, 12.52, 9.80 and 9.83, respectively (59). For this reason, formamidinedisulfide might be expected to exist as the diprotonated salt, rather than the free base, and this has been confirmed in both the solid state (60,61) and in aqueous solution (62).

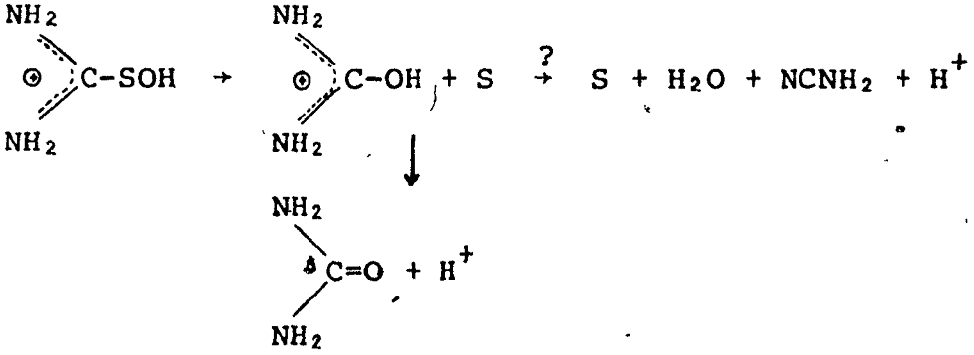
(ii) S-alkyl-isothiouronium salts are decomposed by base to give the thiol and cyanamide (63). Arndt et al (64) prepared the free base S-methyl-isothiourea by condensing MeSH with cyanamide in ether. The compound was found to be strongly basic and decomposed in the solid state within a day at 0°C.

(iii) The rate of decomposition of the disulfide is strongly affected by pH (62), a behaviour not suggested by Toennies' mechanism (58).

(iv) If protonation is taken into account in reactions 2 and 3, the reactions would be more likely to yield urea than cyanamide

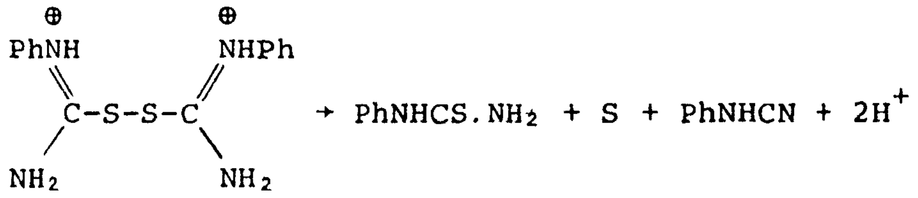


(4)



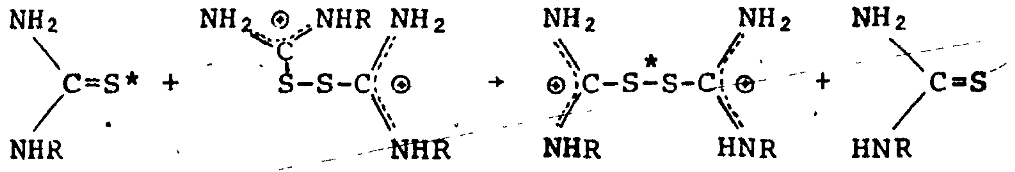
(5)

The formation of sulfur during decomposition of disulfides derived from thioureas was confirmed by Fichter and Wenk (65) and by Fichter and Braun (66), who prepared several N-alkyl formamidinedisulfides by electrolytic oxidation of the corresponding thioureas at a stationary platinum anode. It was found that the N-alkyl compounds were reasonably stable, whereas N-arylformamidinedisulfides were too unstable to be isolated from acid solution without appreciable decomposition, e.g.,



(6)

D'Angeli and Iliceto (67) attempted a study of isotopic exchange of ^{35}S labelled N-alkylthioureas and N-alkylformamidinedisulfides in aqueous solution. They found the exchange to be too rapid for kinetic study. The exchange mechanism was given as a nucleophilic displacement reaction at the disulfide bond



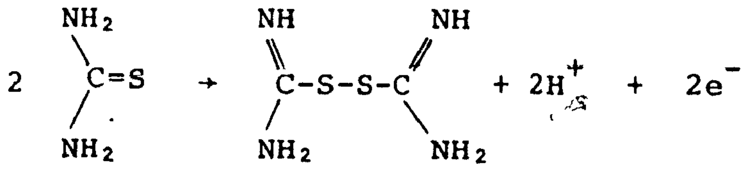
(7)

The redox potential of the formamidiniumdisulfide-thiourea couple has been found to obey the Nernst equation

$$E_{D/Tu} = E^{O}_{D/Tu} + \frac{RT}{2F} \ln \frac{[D]}{[Tu]^{2}} \qquad (8)$$

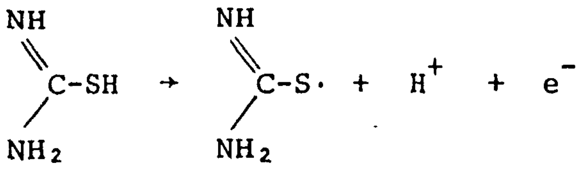
where D and Tu represent the formamidinium-disulfide ion and thiourea respectively, with a standard electrode potential of $E^{O} \simeq +0.42V$ at 25°C (62,68,69). The anodic oxidation of thiourea at a stationary platinum electrode in various supporting electrolytes conforms to a one-electron oxidation of thiourea at pH ~ 1, presumably to give salts of formamidine-disulfide, although no attempt was made to isolate and identify the oxidation product (70). A supporting electrolyte of pH < 3 was required for satisfactory behaviour, but its role was not evident.

Subsequently, it was proposed (71) that the overall reaction was



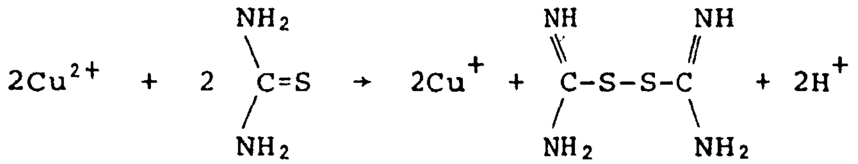
$$2\,(NH_2)_2C{=}S \rightarrow (NH_2)(HN{=})C{-}S{-}S{-}C({=}NH)(NH_2) + 2H^{+} + 2e^{-} \qquad (9)$$

The charge transfer process was assumed to involve the tautomeric thiol form of thiourea,



$$\mathrm{HN{=}C(NH_2){-}SH} \rightarrow \mathrm{HN{=}C(NH_2){-}S\cdot} + H^+ + e^- \qquad (10)$$

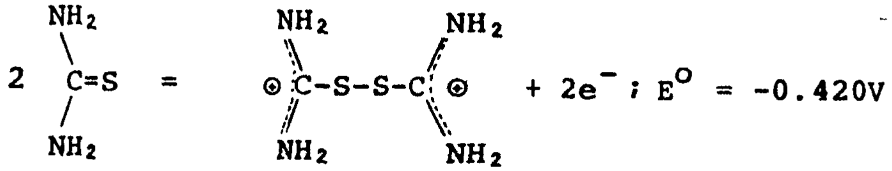
Studies of thiourea as a brightening agent in copper electrodeposition from acid copper sulfate solutions have led to the view that the oxidation of thiourea by cupric ion may be represented (36-39).



$$2Cu^{2+} + 2\,(NH_2)_2C{=}S \rightarrow 2Cu^+ + HN{=}C(NH_2){-}S{-}S{-}C(NH_2){=}NH + 2H^+ \qquad (11)$$

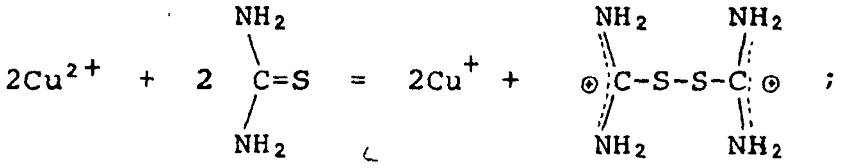
A slow decrease of pH upon addition of thiourea to a weakly acid (pH = 3 to 4) copper sulfate solution has been regarded as confirmation of the mechanism (38). However, it not only disregards protonation of the disulfide, but apparently corresponds to a positive value of ΔG, calculated from the electrode potentials for the two redox couples;

$$Cu^{2+}_{aq} + e^- = Cu^+_{aq} \;;\; E^o = +\,0.167V \qquad (12)$$



$$2\,(NH_2)_2C{=}S = {}^{\oplus}(NH_2)_2C{-}S{-}S{-}C(NH_2)_2{}^{\oplus} + 2e^-\,;\ E^o = -0.420V \qquad (13)$$

Hence



$$2Cu^{2+} + 2\,(NH_2)_2C{=}S = 2Cu^{+} + {}^{\oplus}(NH_2)_2C{-}S{-}S{-}C(NH_2)_2{}^{\oplus} \; ; \qquad (14)$$

$$E^{o} = 0.334 - 0.420 = -0.086$$

This can be seen from the following considerations: the free energy change for reaction 14 (a proper representation of reaction 11 to correspond to experimental observations) may be calculated from

$$\Delta G = 2 \cdot \Delta G_{Cu^{2+}/Cu^{+}} - \Delta G_{D/Tu} \qquad (15)$$

Since

$$\Delta G_{Cu^{2+}/Cu^{+}} = -FE_{Cu^{2+}/Cu^{+}} = -F(0.167 + \frac{RT}{F}\ln\frac{[Cu^{2+}]}{[Cu^{+}]} \qquad (16)$$

and

$$\Delta G_{D/Tu} = -2FE_{D/Tu} = -2F(0.420 + \frac{RT}{2F}\ln\frac{[D]}{[Tu]^{2}} \qquad (17)$$

it follows that

$$\Delta G = 2F(E_{D/Tu} - E_{Cu^{2+}/Cu^{+}}) \qquad (18)$$

Reaction 14 can only proceed as written when $\Delta G \leq 0$ or $E_{Cu^{2+}/Cu^{+}} \geq E_{D/Tu}$. If only cupric ion and thiourea are present initially, values of $E_{Cu^{2+}/Cu^{+}}$ and $E_{D/Tu}$ may be calculated from the extent of reaction. For the initial conditions at t = 0 of [thiourea]^{o} = [Tu]^{o},

[formamidiniumdisulfide]^{o} = [D]^{o} = 0, [cupric ion^{2+}]^{o} = [Cu^{2+}]^{o}

and [cuprous ion^{+}] = [Cu^{+}]^{o} = 0, oxidation of the fraction

$$x = \frac{[Tu]^{o} - [Tu]}{[Tu]^{o}}$$

of the thiourea corresponds to reduction of

$$x = \frac{[Cu^{2+}]^{o} - [Cu^{2+}]}{[Cu^{2+}]^{o}}$$

7

of the cupric ion. For this extent of reaction the potentials of the two couples may be written

$$E_{D/Tu} = +\ 0.420 + \frac{RT}{2F} \ln \frac{x}{(1-x)^2} - \frac{RT}{2F} \ln 2\,[Tu]^{o} \quad (19)$$

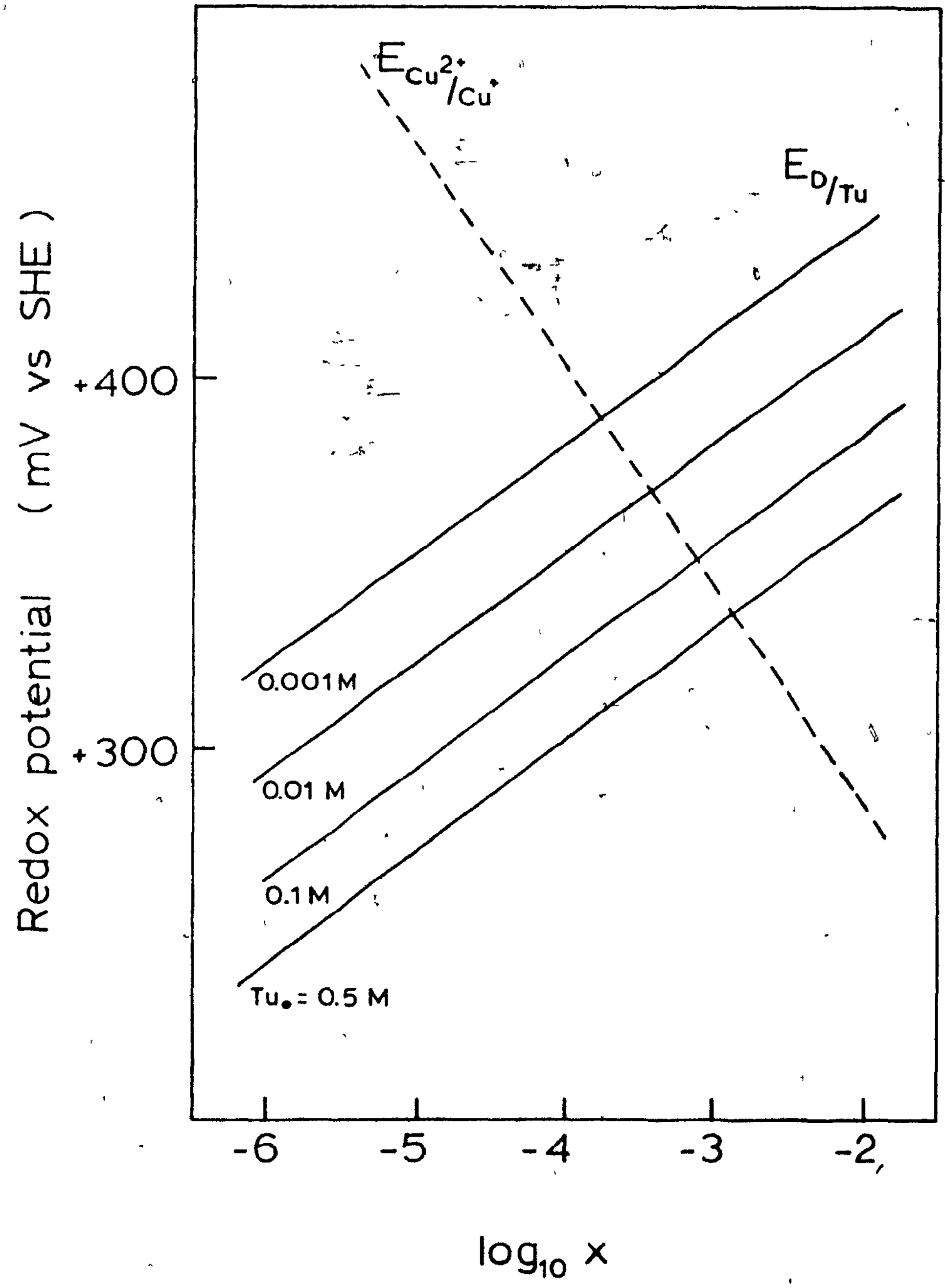
and

$$E_{Cu^{2+}/Cu^{+}} = +\ 0.167 + \frac{RT}{F} \ln \frac{(1-x)}{x} \quad (20)$$

FIGURE 1

VARIATION OF THE REDOX POTENTIALS OF THE COUPLES D/Tu and Cu^{2+}/Cu^{+} CALCULATED FOR EXTENT OF REACTION, X, ACCORDING TO EQNS. 19 AND 20

NOTE: For any given initial concentration of thiourea, the maximum extent of reaction is given by the value of x at which the line representing the change in $E_{Cu^{2+}/Cu^{+}}$ with x intersects the corresponding line for $E_{D/Tu}$ for that initial concentration of thiourea.



$E_{Cu^{2+}/Cu^{+}}$
$E_{D/Tu}$
0.001 M
0.01 M
0.1 M
Tu_o = 0.5 M
+400
+300
Redox potential (mV vs SHE)
-6
-5
-4
-3
-2
$\log_{10} x$

When $E_{D/\widetilde{Tu}}$ and $E_{Cu^{2+}/Cu^{+}}$ are plotted as functions of x, (Figure 1), it becomes evident that a significant conversion [> ½%] of thiourea to disulfide according to reaction 14 is not possible, since ΔG becomes positive.

A more satisfactory stoichiometry for the oxidation of thiourea by cupric ion in aqueous solution appears to be possible by considering the fact that thiourea forms strong complexes with cuprous ions (72,73). The potential of the cupric-cuprous couple in the presence of thiourea must therefore be written to take into account the equilibria

$$Cu\,Tu^{+} \underset{=}{\overset{}{K_1}} Cu^{+} + Tu \qquad (21)$$

$$Cu\,Tu_2^{+} \underset{=}{\overset{}{K_2}} Cu\,Tu^{+} + Tu \qquad (22)$$

$$Cu\,Tu_3^{+} \underset{=}{\overset{}{K_3}} Cu\,Tu_2^{+} + Tu \qquad (23)$$

$$Cu\,Tu_4^{+} \underset{=}{\overset{}{K_4}} Cu\,Tu_3^{+} + Tu \qquad (24)$$

$$Cu\,Tu_4^{+} \underset{=}{\overset{}{\beta_4}} Cu^{+} + 4Tu \qquad (25)$$

where $\beta_4 = K_1 K_2 K_3 K_4 \simeq 3 \times 10^{-16}$ (74,75). Under typical electroplating conditions, with low thiourea concentrations, only equilibrium 21 need be considered for a first approximation, and

$$E_{Cu^{2+}/Cu^{+}} = +\,0.167 - \frac{RT}{F}\ln K_1 + \frac{RT}{F}\ln\frac{[Cu^{2+}][Tu]}{[Cu\ Tu^{+}]} \qquad (26)$$

where

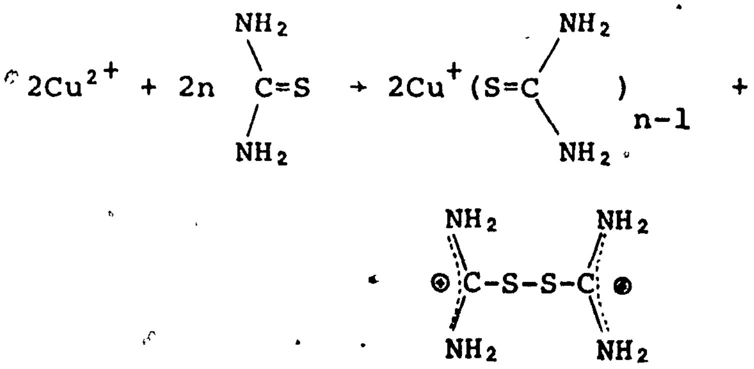
$$K_1 \simeq \overline{K} = \beta_4^{1/4} \qquad (27)$$

i.e., $K_1 \simeq 1.32 \times 10^{-4}$

Hence

$$E_{Cu^{2+}/Cu^{+}} = +\,0.167 + 0.230 + \frac{RT}{F}\ln\frac{[Cu^{2+}][Tu]}{[Cu\ Tu^{+}]} \qquad (28)$$

The effective potential of the cupric-cuprous couple is thus significantly increased in the presence of thiourea, making the oxidation of thiourea by cupric ion a thermodynamically favorable reaction. In general agreement with Slashcheva et al (76) and Shulman et al (77), the stoichiometric equation for oxidation of thiourea by cupric ion in aqueous solution would therefore be



$$2Cu^{2+} + 2n\,(NH_2)_2C{=}S \rightarrow 2Cu^{+}(S{=}C(NH_2)_2)_{n-1} + {}^{\oplus}(NH_2)_2C{-}S{-}S{-}C(NH_2)_2{}^{\oplus} \qquad (29)$$

with

$$2 \leq n \leq 5$$

Although they are not directly relevant to the present investigation, it is interesting, perhaps, to note that studies have been made of the oxidation of thiourea in acid solutions to formamidinedisulfide, using ceric (78) and cobaltic (79) ions and of the oxidation of cuprous-thiourea complexes by cupric perchlorate in acetonitrile (80), in which the disulfide was represented as the free base in solution.

EXPERIMENTAL AND RESULTS

EQUIPMENT

Spectra were recorded on a Perkin-Elmer 402 UV visible spectrophotometer fitted with a thermostatted cell holder. The wavelength and absorbance scales were checked using didyimium and Holmium glass filters and standard potassium chromate solution (NBS(US) Circular 484 (1949)) respectively. The cells used were fused quartz having a path length of 10 mm and completely transparent over the range studied (190 - 850 nm).

Infrared spectra were recorded as nujol or perfluorokerosene mulls on a Perkin-Elmer 337 Grating IR spectrophotometer at a scan rate of 20 minutes for each of the

4000 - 1200 cm^{-1} and 1330 - 400 cm^{-1} ranges. Polystyrene film (0.05 mm) was used for wavenumber calibration.

Potential and pH measurements were made relative to a saturated calomel reference electrode, using an Orion model 701 digital millivolt/pH meter.

MATERIALS

Water used in preparing all solutions was deionized and distilled. Thiourea (Baker analyzed reagent) and tetramethylthiourea (Eastman) were used without further purification. Sulfuric acid (Anachemia, Reagent grade, 96%) and hydrogen peroxide (Fisher certified reagent, 30%) were used as supplied. Cupric sulfate pentahydrate (Fisher certified reagent) was once recrystallized from acidified distilled water to remove insoluble impurities. Solutions of acids and sodium hydroxide were standardized against mercuric oxide and acid potassium phthalate, respectively.

OXIDATION OF THIOUREA WITH HYDROGEN PEROXIDE

Thiourea (15.22 g = 0.2 moles) was dissolved in 50% aqueous ethanol (200 ml) containing sulfuric acid (5.8 ml 96% H_2SO_4 = 0.1 mole). The solution was cooled below + 5°C in ice water, and 30% hydrogen peroxide (10.8 ml = 0.1 mole) added with vigorous stirring over a period of five minutes. A heavy white precipitate of formamidinedisulfide sulfate was formed almost immediately, and collected after 20 minutes on a sintered glass funnel by suction filtration. It was washed successively with 4 x 20 ml cold 50% ethanol, 40 x 20 ml 95% ethanol and 5 x 20 ml anhydrous diethyl ether. Finally, it was dried by drawing filtered air through it for six hours.

The disulfide was weighed and stored in a vacuum desiccator over indicating silica gel. In successive preparations the yield was 23 ± 1 g (six preparations) representing about 90% of theoretical. More disulfide could be recovered from the mother liquor, to bring the yield to 98%.

The formamidiniumdisulfide sulfate was obtained as a dense white powder (microscopic needles) soluble in dilute acid at 25°C to the extent of ≃ 2.5 g/100 ml; it was insoluble in ethanol. All samples prepared melted with decomposition at 135-136°C (uncorrected). The reaction with picric acid gave a yellow insoluble picrate that melted with decomposition at 158-159°C (uncorrected), which compared favourably with a value of 154°C given by Werner (57).

Elemental analyses by Schwarzkopf Microanalytical Laboratory are shown in Table I, along with values for the titratable acid, sulfate and total sulfur contents obtained independently.

Previous preparations of a sulfate of formamidinedisulfide (53,65) were claimed to be the anhydrous salt on the basis of total sulfur and sulfate analyses. Melting points were not recorded for these preparations. The present preparations gave an absorption at ~ 3500 cm^{-1} in the infrared which could be attributed to an OH stretching mode, presumably indicative of a hydrated salt. Upon deuteration this band shifted to ~ 2600 cm^{-1}, giving a frequency ratio of 1.35 in good agreement with the theoretical isotope effect of 1.37. However, attempts to show the presence of water by weight loss over silica gel in a vacuum desiccator failed. In 10 days, 21.6 g of the finely powdered sulfate lost only 5.6 mg, representing 0.38% of the weight loss calculated for the complete dehydration of a formamidiniumdisulfide sulfate monohydrate.

Accordingly, the formula weight of the sulfate was determined by UV spectroscopy.

In aqueous solution, the disulfide showed no absorption maximum above 190 nm, and only a continually increasing absorption toward the vacuum UV region. The UV maximum at 204 nm given by Hintermann and Javet (37) did not appear.*

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* It is possible that this observation was caused by excessive stray light in a common error in the lower wavelength region of interest. Spectra of the disulfide taken with a Unicam SP 800 showed a concentration dependent maximum in the region 200-210 nm, but similar distortion of the spectrum of thiourea showed this maximum for the disulfide to be an instrumental artifact.

Since Foss et al (60) have shown that formamidinedisulfide dihydrochloride is free from water of crystallization, a sample of the chloride was prepared and its infrared spectrum taken. No evidence was found that it contained water of crystallization. Beer's law was verified for solutions of the dihydrochloride in 0.4 M HCl at 25°C and the molar absorptivity found to be 1844 ± 22 ℓ $mole^{-1}$ cm^{-1} at 236.0 nm. Beer's law was then verified for solutions of the sulfate in 0.4 M HCl at 25°C and the absorptivity was 6.92 ± 0.08 ℓ g^{-1} cm^{-1} at 236.0 nm. Combination of these two values gives a formula weight for formamidiniumdisulfide sulfate of 266 ± 4, in good agreement with the formula weight of 266.34 required for a monohydrate. The total sulfur content corresponds to a formula weight for the sulfate of n x (83.3 ± 0.3), or 265 ± 1 for n = 3. The constitution of the formamidiniumdisulfide sulfate as a monohydrate is thus established with reasonable certainty.

The infra-red, Raman and UV spectra of formamidiniumdisulfide sulfate monohydrate are shown in Figures 2,3 and 4, respectively. The infra-red spectrum of the deuterated compound is shown in Figure 5.

OXIDATION OF THIOUREA WITH ACID COPPER SULFATE

Thiourea (76.13 g = 1 mole) was dissolved in warm (40°C) 1 M H_2SO_4 (800 ml) in a two liter beaker. The solution was rapidly stirred with a teflon-coated magnetic bar,

FIGURE 2

INFRARED ABSORPTION SPECTRUM OF FORMAMIDINIUMDISULFIDE SULFATE MONOHYDRATE

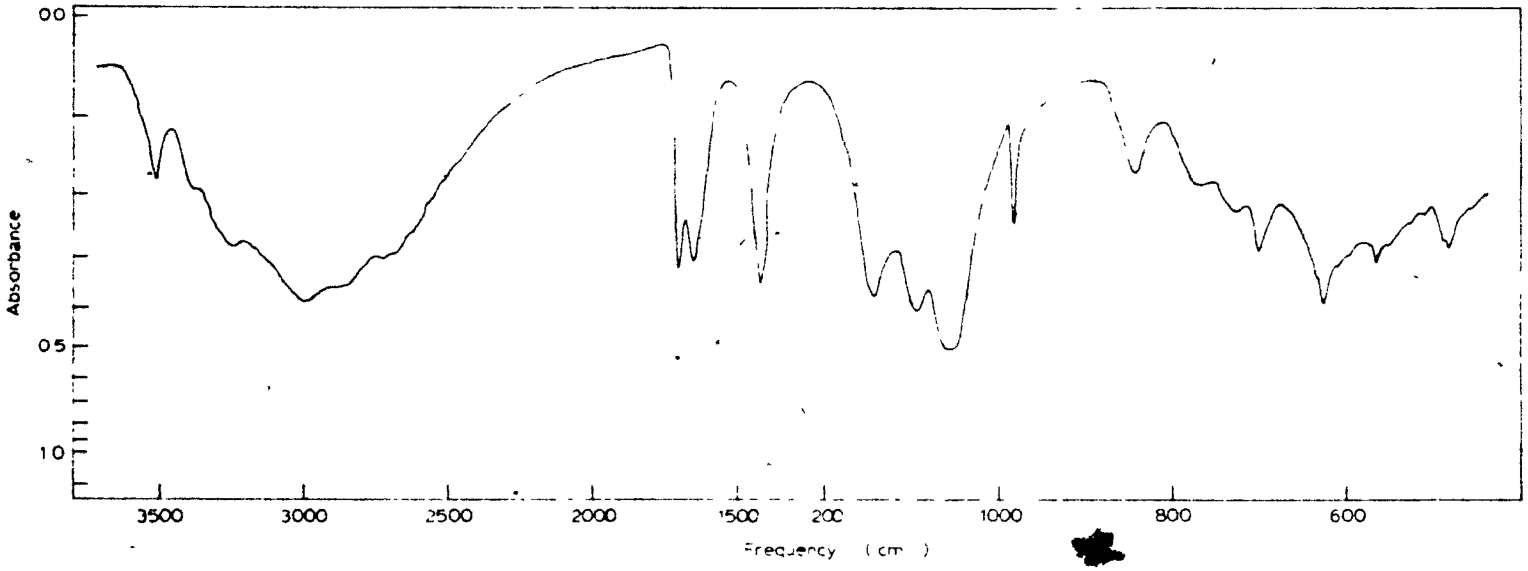
Absorbance
0.0
0.5
1.0
3500
3000
2500
2000
1500
200
1000
800
600
Frequency (cm)

FIGURE 3

RAMAN SPECTRUM OF FORMAMIDINIUMDISULFIDE SULFATE MONOHYDRATE *

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* Determined by Dr. G. Barna
Dept. of Chemistry

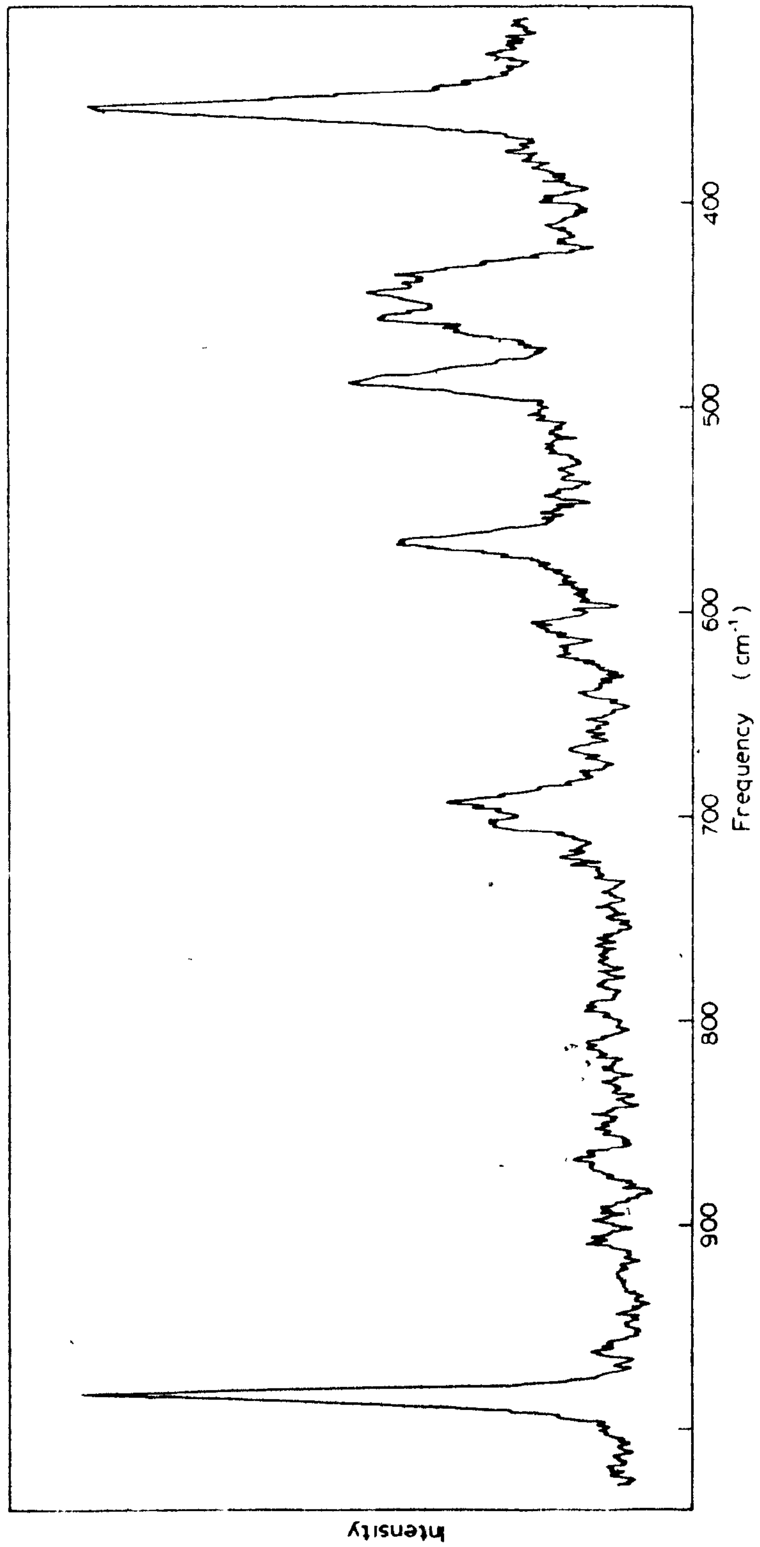

Intensity
Frequency (cm^{-1})
400
500
600
700
800
900

FIGURE 4

UV ABSORPTION SPECTRUM OF FORMAMIDINIUM-DISULFIDE SULFATE MONOHYDRATE IN 0.4 M HCl

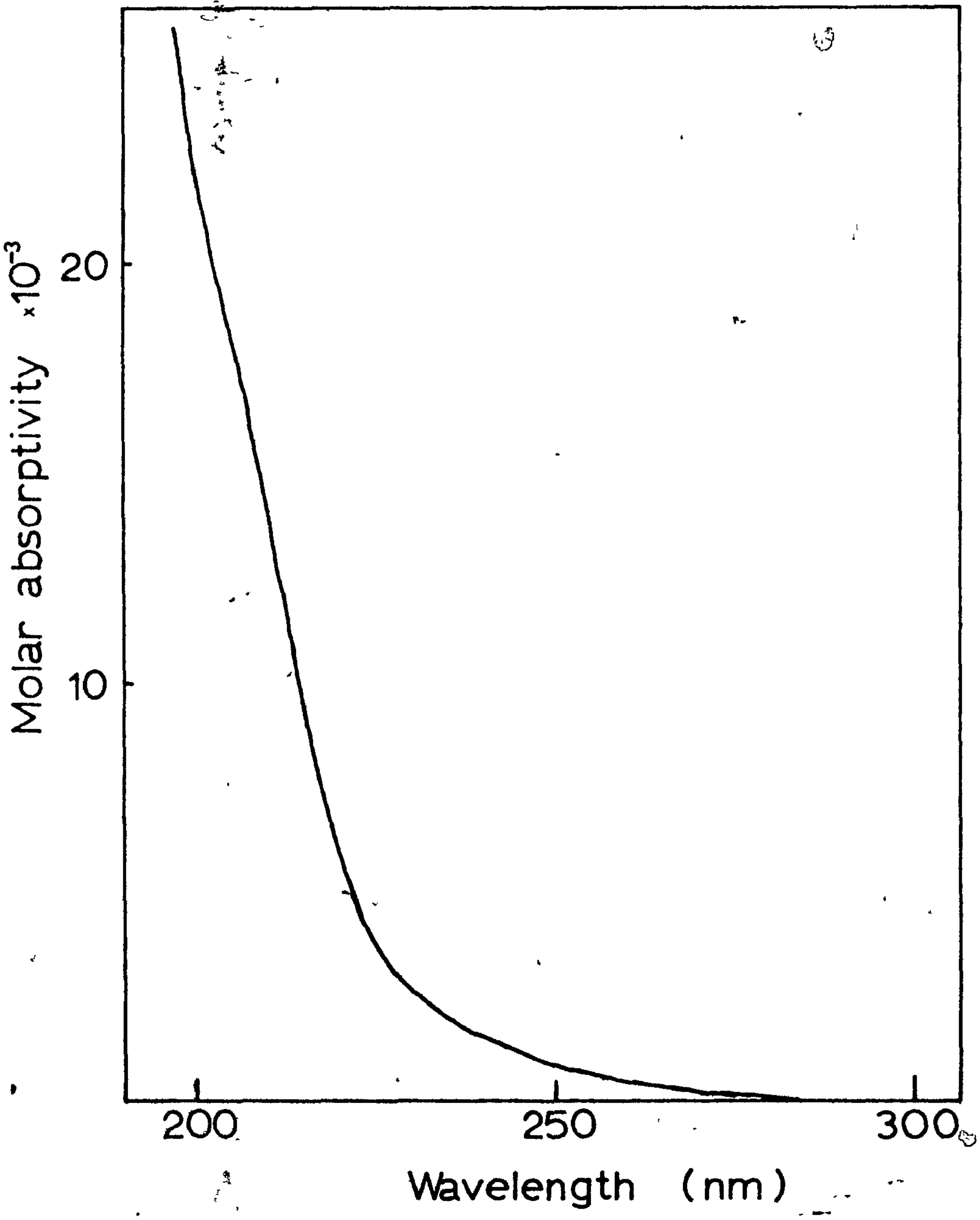
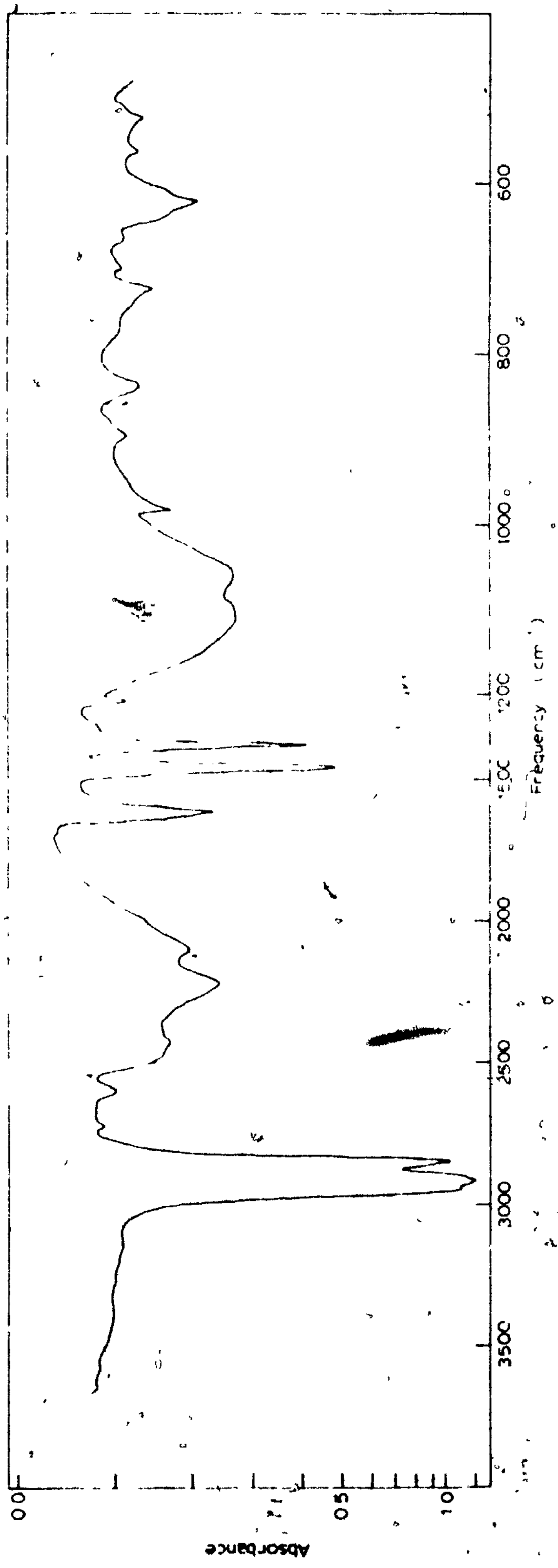

Molar absorptivity ×10^{-3}
20
10
200
250
300
Wavelength (nm)

FIGURE 5

INFRARED ABSORPTION SPECTRUM OF FULLY DEUTERATED FORMAMIDINIUMDISULFIDE SULFATE MONOHYDRATE AS A NUJOL MULL



Absorbance
0.0
0.5
1.0
Frequency (cm⁻¹)
600
800
1000
1200
1600
2000
2500
3000
3500

TABLE I

ANALYSIS OF FORMAMINIDIUMDISULFIDE SULFATE MONOHYDRATE *

A: ELEMENTAL ANALYSIS BY SCHWARZKOPF MICROANALYTICAL LABORATORIES			
Element %	H_2O_2-Oxidation	$CuSO_4$-Oxidation	Calculated
S	36.80	36.23	36.12
C	9.63	9.20	9.01
N	21.84	20.94	21.02
H	4.04	4.07	3.78
B: TOTAL SULFUR, SULFATE AND TITRATABLE ACIDITY			
S(total)	36.34 ± 0.14		36.12
SO_4	37.57 ± 0.28		36.08
H^+	0.772 ± 0.009		0.757

* Calculated values are for $(H_4N_2CS-)_2SO_4.H_2O$ with a formula weight of 266.34

and acid copper sulfate solution slowly added until it was in slight excess, as indicated by a faint blue color. A mixture of insoluble cuprous thiourea complexes separated as an oil after a few minutes. The solution was decanted after one hour and allowed to stand in ice water over night to ensure complete crystallization of any remaining cuprous-thiourea salts. It was then filtered and diluted with an equal volume of cold 95% ethanol. The white precipitate that formed was filtered after one hour and washed successively with 50% ethanol, 95% ethanol and anhydrous diethyl ether. The air-dried yield (24 hr) was 32.0 g (=0.12 mole $(H_4N_2CS-)_2SO_4.H_2O$), with a melting point of 135-136°C. The picrate melted at 159°C. The infrared and UV spectra of the sulfate of formamidinedisulfide obtained by cupric ion and by peroxide oxidation were shown to be identical.

Elemental analyses are shown in Table I.

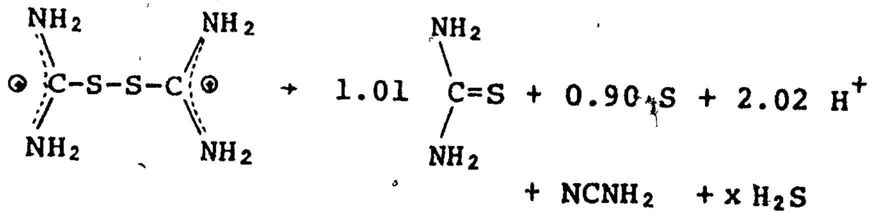
STOICHIOMETRY OF THE HYDROLYSIS OF FORMAMIDINEDISULFIDE

When the sulfate of formamidinedisulfide was dissolved in neutral solution a very rapid initial decrease in pH was followed by a more gradual change. When the disulfide was added to dilute acid of pH 2.5 to 3.0 there was only a slow decrease in pH, the rate of which changed with time and concentration of disulfide initially added (Figure 6). From the immediate pH change caused by dissolving disulfide in dilute acid (i.e., negligible pH change due to the hydrolysis reaction, see Figure 6) a lower limit can be estimated for the effective pK_a of the formamidiniumdisulfide ion as

$$pK_a \geq 6$$

Surprisingly, the release of enough acid to account for 10% decomposition of one gram of formamidiniumdisulfide sulfate monohydrate caused no turbidity in the solution (100 ml), whereas the Toennies mechanism predicted that 0.012 g of elemental sulfur should have been formed.

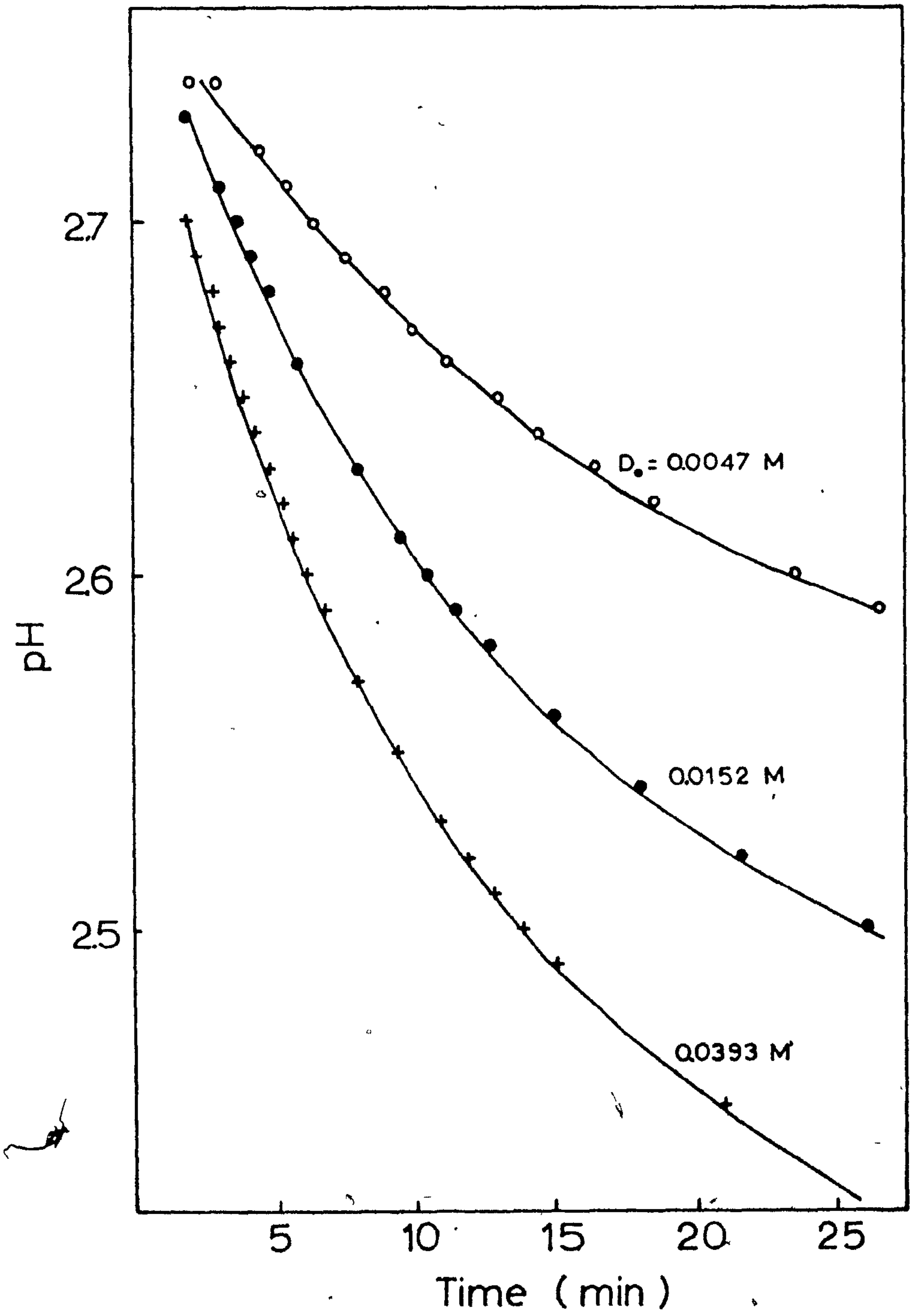
Treatment of the disulfide dissolved in a known amount of 1.000 N HCl with excess 1.000 N NaOH gave immediate precipitation of amorphous sulfur. Typically, 1.0191 g $(H_4N_2CS-)_2SO_4H_2O$ (=0.00383 moles) dissolved in 10.00 ml 1 N HCl and treated with 25.00 ml 1 N NaOH gave 0.1104 g amorphous sulfur (0.00344 gatom), 0.00389 moles thiourea (Argentimetric, "Cyanamide", American Cyanamide Co. p.23) and 0.00775 equivalents H^+. Hydrogen sulfide was detectable by its odor and the presence of cyanamid was demonstrated qualitatively by formation of the yellow silver salt in the ether extract of the decomposition products. This would indicate a decomposition according to



$$(NH_2)_2\overset{\oplus}{C}\text{-}S\text{-}S\text{-}\overset{\oplus}{C}(NH_2)_2 \rightarrow 1.01\ (NH_2)_2C{=}S + 0.90\ S + 2.02\ H^+ + NCNH_2 + x\,H_2S \qquad (30)$$

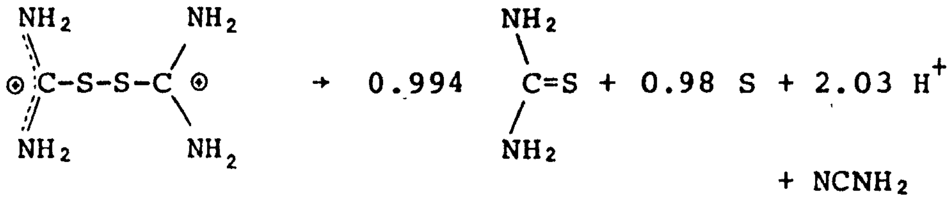
FIGURE 6

DECREASE IN pH CAUSED BY HYDROLYSIS OF FORMAMIDINIUMDISULFIDE SULFATE MONOHYDRATE IN HYDROCHLORIC ACID WITH AN INITIAL pH OF 2.73



pH
2.7
2.6
2.5
D_0 = 0.0047 M
0.0152 M
0.0393 M
5
10
15
20
25
Time (min)

Addition of a weighed quantity of the disulfide sulfate monohydrate to boiling distilled water gave similar results except that no hydrogen sulfide was detectable. Thus, 10.3672 g of the compound (= 0.0389 mole) added to ~ 200 ml boiling distilled water gave 1.2253 g amorphous sulfur (=0.0382 gatom), 0.0387 moles thiourea, 0.0790 equivalents of H^+ and cyamide. This stoichiometry also conforms quite well to the stoichiometry proposed by Toennies,



$$(NH_2)_2\overset{\oplus}{C}-S-S-\overset{\oplus}{C}(NH_2)_2 \rightarrow 0.994\ (NH_2)_2C=S + 0.98\ S + 2.03\ H^+ + NCNH_2 \qquad (31)$$

When a weighed quantity of the disulfide sulfate was added to distilled water at 25°C and slowly heated to effect decomposition, the amount of thiourea obtained increased significantly to 1.31 ± 0.05 moles per mole of the parent compound (5 determinations). The titratable acid remained at 2.04 ± 0.02 equivalents per mole of disulfide sulfate. Amorphous sulfur and cyanamide were also obtained but were not determined quantitatively.

To determine the stoichiometry corresponding to decomposition of the disulfide at the concentrations anticipated in electroplating baths ($< 10^{-3}$ M) a more sensitive analytical method was needed. While recording the UV spectra of formamidinedisulfide, it had been observed that the absorbance of a freshly prepared solution was unaffected by pH in the range 0.05 to 4.00 M H_2SO_4, but the solutions all showed a gradual increase in absorbance at ~ 236 nm, as shown in Figure 7.Since thiourea was known to be the major hydrolysis product, its UV absorbance was determined (Figure 8).It was found to possess absorbance maxima at 196 nm ($\log_{10}\varepsilon$=4.088 ± 0.005) and 236 nm ($\log_{10}\varepsilon$=4.076 ± 0.004) and to obey Beers law over the whole range studied. The conversion of the disulfide sulfate monohydrate to thiourea and other products in aqueous solution would therefore correspond to an increase in absorbance in the region about 236 nm.

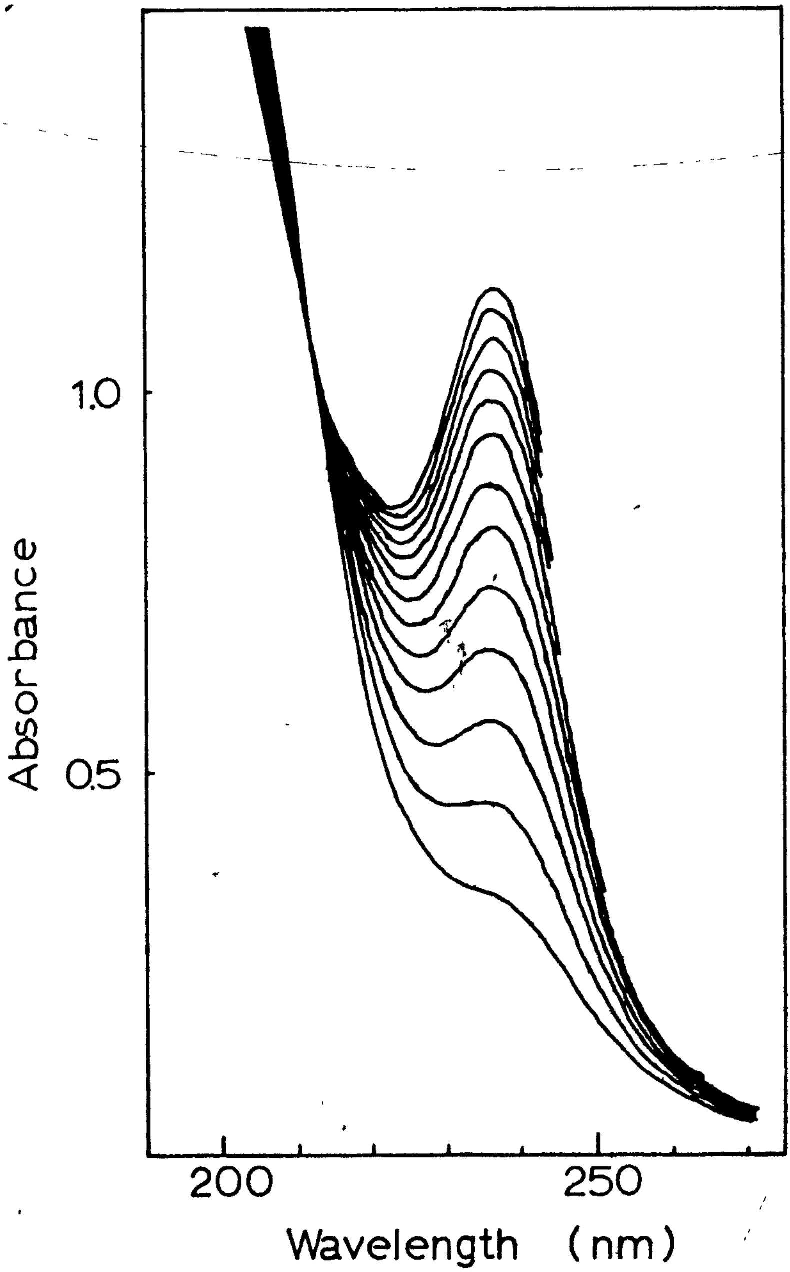
As shown in Fig. 7 and observed in all the decompositions studied by UV spectrophotometry, the mixture of disulfide and its decomposition products appears to possess an isobestic point at 211 nm. This indicates that decomposition occurs without interference from side reactions under these experimental conditions.

The absorbance of the disulfide and its decomposition products at any time, t, and wavelength λ, can be written as the sum of the individual absorbances, expressed in terms of the product of molar absorptivity $\varepsilon_{i.x}$ and concentration $[C_i]_t$ for each species i,

$$A_{\lambda,t} = \varepsilon_{D,\lambda}[D]_t + \varepsilon_{Tu,\lambda}[Tu]_t + \sum_i \varepsilon_{i,\lambda}[C_i]_t \qquad (32)$$

FIGURE 7

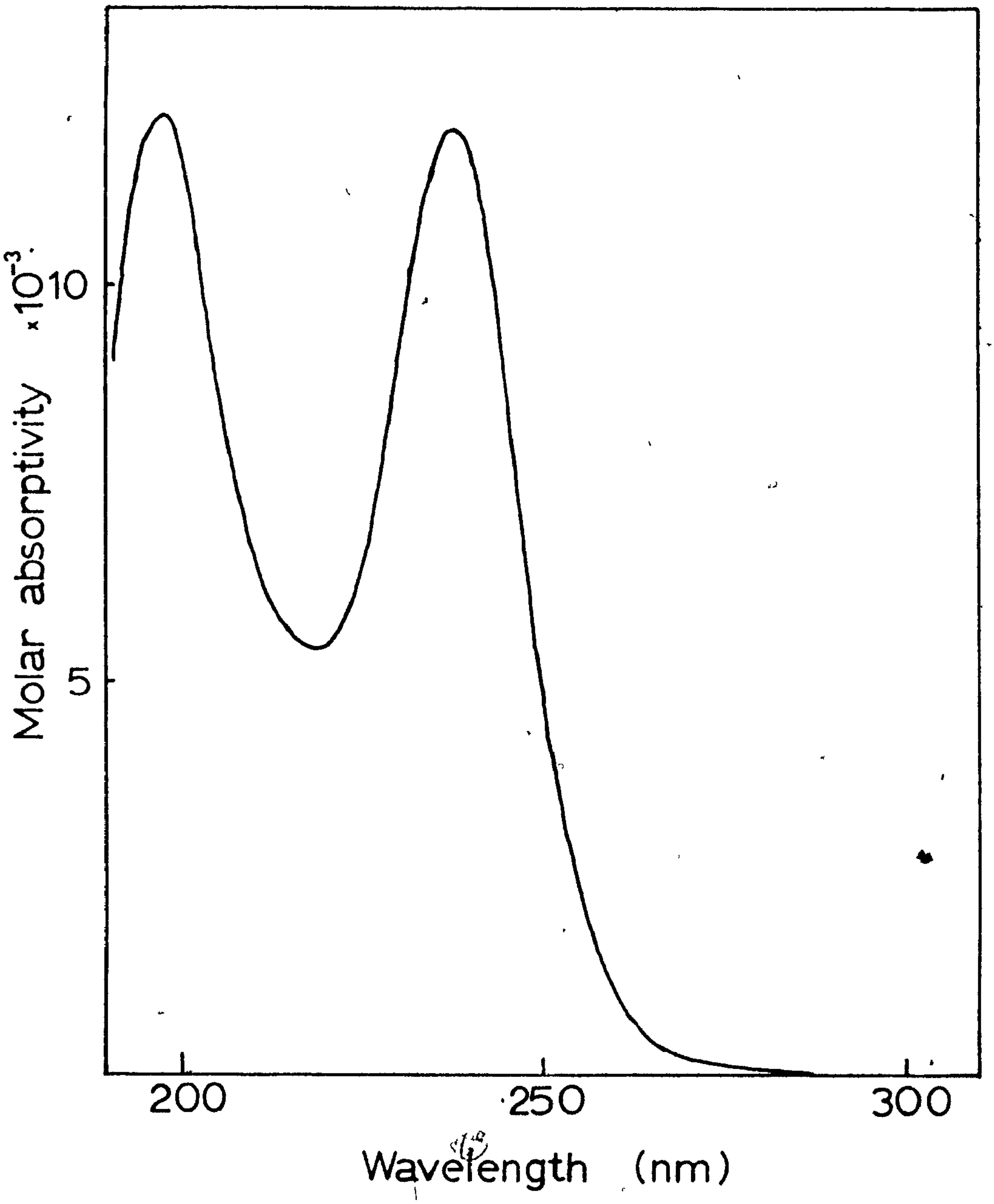
INCREASE IN THE ABSORBANCE AT 236 nm
OF A DILUTE ACID SOLUTION OF FORMAMIDINIUMDISULFIDE UNDERGOING SLOW HYDROLYSIS



Absorbance
1.0
0.5
200
250
Wavelength (nm)

FIGURE 8

UV ABSORPTION SPECTRUM OF THIOUREA
IN AQUEOUS SOLUTION AT pH = 7


Molar absorptivity ×10⁻³
10
5
200
250
300
Wavelength (nm)

where the summation $\sum_i \varepsilon_{i,\lambda} C_{i,t}$ represents as yet, unidentified decomposition products. Because of the relatively simple structure of the disulfide, the possible products are probably limited to cyanamide, urea, formamidinesulfenic acid, formamidinesulfinic acid, formamidinesulfonic acid, ammonium thiocyanate (doubtful), and possibly 1,1'-thiodiformamidine formed by reaction of thiourea with cyanamide.

Cyanamide and urea have essentially no absorbance above 210 nm and present no difficulty to the spectrophotometric detection of other possible products. The possible presence of sulfenic acids may be neglected, since they are known to be highly reactive, and generally undergo rapid disproportionation if no other reactant is available. However, formamidinesulfinic acid, which is relatively stable* in dilute acid and has an extinction coefficient < 500 at 230 nm, could be formed from sulfenic acid. Formamidinesulfonic acid is very unstable (82) and could possibly arise from disproportionation of formamidinesulfinic acid. Thiourea will readily condense with cyanamide in ethanol to form salts of

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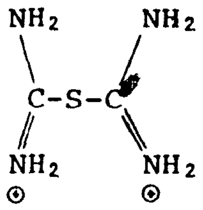
* Attempts to isolate formamidinesulfinic acid as a product of the hydrolysis of formamidinedisulfide did not succeed, presumably because of hydrolysis of the former (81).

1,1'-thiodiformamidine



but this compound was found to be much more susceptible to hydrolysis than the disulfide, so that it should not form in the systems under consideration.

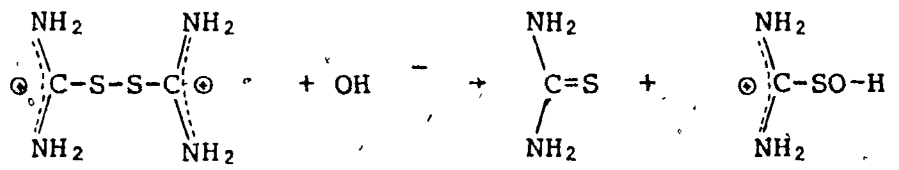
Since none of the compounds considered could contribute appreciably to the absorbance of the disulfide and its decomposition products at wavelengths greater than 230 um, the absorbance may be represented

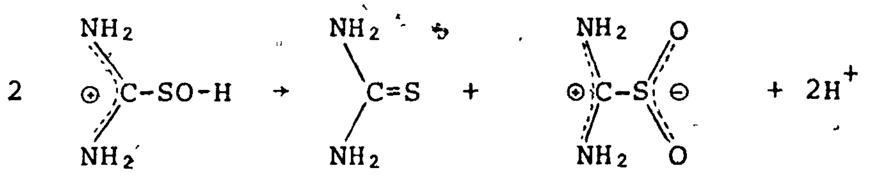
$$A_{\lambda \geq 230\text{nm},t} \cong \varepsilon_{D,\lambda}\,[D]_t + \varepsilon_{Tu,\lambda}\,[Tu]_t \qquad (33)$$

or at such a time when all disulfide can be assumed to be decomposed

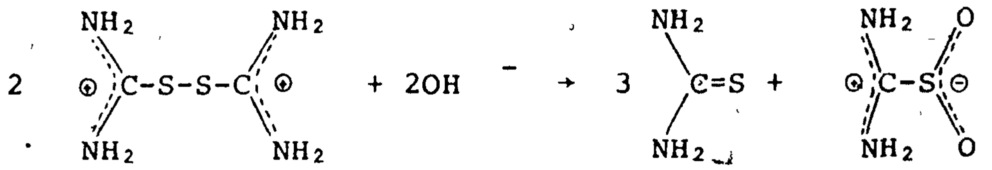
$$A_{\lambda \geq 230\text{nm},t=\infty} \cong \varepsilon_{Tu,\lambda}\,[Tu] \qquad (34)$$

Eqn. (34) and $\varepsilon_{236} = 11900 \pm 100$ for thiourea were used to estimate the amount of thiourea produced in the decomposition of the disulfide sulfate monohydrate in aqueous solution at 25 ± 5°C. Over the range of initial disulfide concentrations from 1×10^{-6} to 3×10^{-4} M the final absorbance at 236 nm gave 1.34 ± 0.07 moles of thiourea per mole of disulfide, with individual experiments giving values as high as 1.47. This stoichiometry would be in accord with a reaction sequence involving formamidinesulfenic acid which rapidly disproportionates to give thiourea and formamidinesulfinic acid,


(35)


(36)

The overall stoichiometry would then be


(37)

The stoichiometry represented by eqn. (37) would account for the observed high thiourea to disulfide ratio concomittantly with the production of the two equivalents of acid per mole of disulfide decomposed.

KINETICS OF THE HYDROLYSIS OF FORMAMIDINE DISULFIDE IN DILUTE ACID, pH $\leq$ 4

On the basis of eqns. (32) and (37), the absorbance of a solution of formamidinedisulfide, D, and its decomposition products thiourea, Tu, and formamidinesulfinic acid, S at a given wavelength may be written

$$A_{\lambda,t} = \varepsilon_{D,\lambda} [D]_t + \varepsilon_{Tu,\lambda}[Tu] + \varepsilon_{S,\lambda}[S]_t \qquad (38)$$

At 236 nm, where the difference between the extinction coefficients is greatest,

$$A_{236,t} = 1844\ [D]_t + 11900\ [Tu]_t + 500\ [S]_t \qquad (39)$$

The change in absorbance with time may then be expressed

$$\frac{dA_{236,t}}{dt} = 1844 \frac{d\,[D]_t}{dt} + 11900\ \frac{d\,[Tu]_t}{dt} + 500 \frac{d\,[S]_t}{dt} \qquad (40)$$

From eqn. (37)

$$\frac{d\,[D]_t}{dt} = -\ 0.67\ \frac{d\,[Tu]_t}{dt} \qquad (41)$$

and

$$\frac{d\,[S]_t}{dt} = 0.33\ \frac{d\,[Tu]_t}{dt} \qquad (42)$$

Substitution of these expressions into eqn. (40) gives

$$\frac{dA_{236}}{dt} = -1210\frac{d\,[Tu]_t}{dt} + 1190\frac{d\,[Tu]_t}{dt} + 160\frac{d\,[Tu]_t}{dt} \quad (43)$$

or

$$\frac{dA_{236}}{dt} = (10800 \pm 120)\frac{d\,[Tu]_t}{dt} = R_o \quad (44)$$

Therefore the initial rate of change of absorbance at 236 nm can be linearly related to the rate of the hydrolysis reaction, defined by

$$r = -\frac{1}{2}\frac{d[D]_t}{dt} = +\frac{1}{3}\frac{d\,[Tu]_t}{dt} = \frac{d\,[S]}{dt} = k'[D]^m[HCl]^n \quad (45)$$

Using a Perkin-Elmer 402 UV-visible spectrophotometer in the time drive mode, the initial rate of change of absorbance at 236.0 nm was recorded for the disulfide in HCl of 9.65×10^{-4} M concentration. Measurements were made at 25°C for initial disulfide concentrations over the range 4.60 to 30.07×10^{-5} M. The results are shown in Table 2.

The least-mean-squares slope of the plot of ln R_o against ln D_o (Figure 9)is + 1.06, which indicates that the rate of decomposition of the disulfide is first order in disulfide at constant pH, i.e., m = 1 in eqn. (45).

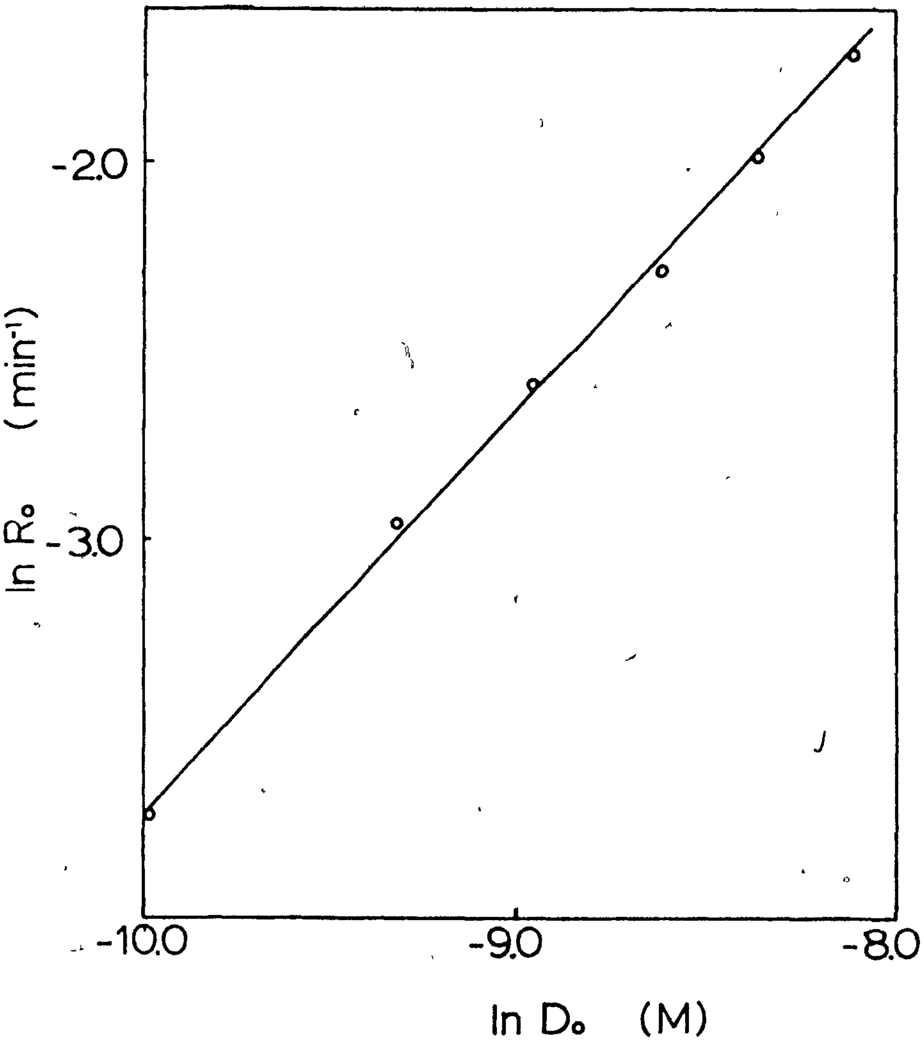
TABLE 2

DEPENDENCE OF THE INITIAL RATE OF HYDROLYSIS ON THE INITIAL DISULFIDE CONCENTRATION AT 25°C IN HCl OF 9.65×10^{-4} M CONCENTRATION

D_o (M)	R_o (M^{-1} cm min^{-1})
0.0000460	0.0238
0.0000899	0.0520
0.0001284	0.0753
0.0001809	0.101
0.0002347	0.136
0.0003007	0.178

FIGURE 9

VARIATION OF INITIAL RATE OF CHANGE OF ABSORBANCE AT 236 nm WITH INITIAL CONCENTRATION OF FORMAMIDINEDISULFIDE IN 0.000965 M HCl AT 25°C.


-2.0
-3.0
ln R₀ (min⁻¹)
-10.0
-9.0
-8.0
ln D₀ (M)

The dependence of R_o upon HCl concentration at constant disulfide concentration ($\sim 2.3 \times 10^{-4}$ M) was similarly determined for a range of acid concentrations from 9.65×10^{-4} to 9.65×10^{-3} M, with the results shown in Table 3 and plotted as ln R_o against ln HCl in Figure 10. Since this plot has a least-mean-squares slope of -1.06, the rate of reaction is apparently related inversely to the concentration of acid, with n = - 1 in eqn. (45).

The rate expression therefore takes the form

$$r = -\frac{1}{2}\frac{d\,[D]_t}{dt} = +\frac{1}{3}\frac{d[Tu]_t}{dt} = +\frac{d[S]_t}{dt} = k'\,[D][HCl]^{-1} \quad (46)$$

with the rate of formation of thiourea given by

$$\frac{d\,[Tu]_t}{dt} = 3\,k\,[D][HCl]^{-1} = \frac{1}{10800}\,\frac{dA_{236}}{dt}$$

Inhibition of the decomposition by hydrochloric acid probably results from a rapid equilibrium involving HCl that precedes the rate determining step of the hydrolysis. Since hydroxide ion is known to decompose some alkyl and aryl-disulfides by nucleophilic attack upon the disulfide bond (83-85), it may be assumed that formamidinedisulfide reacts similarly. Since $[H^+][OH^-] = K_w$ or $[H^+]^{-1} = [OH^-]\,K_w^{-1}$ the rate expression may be written

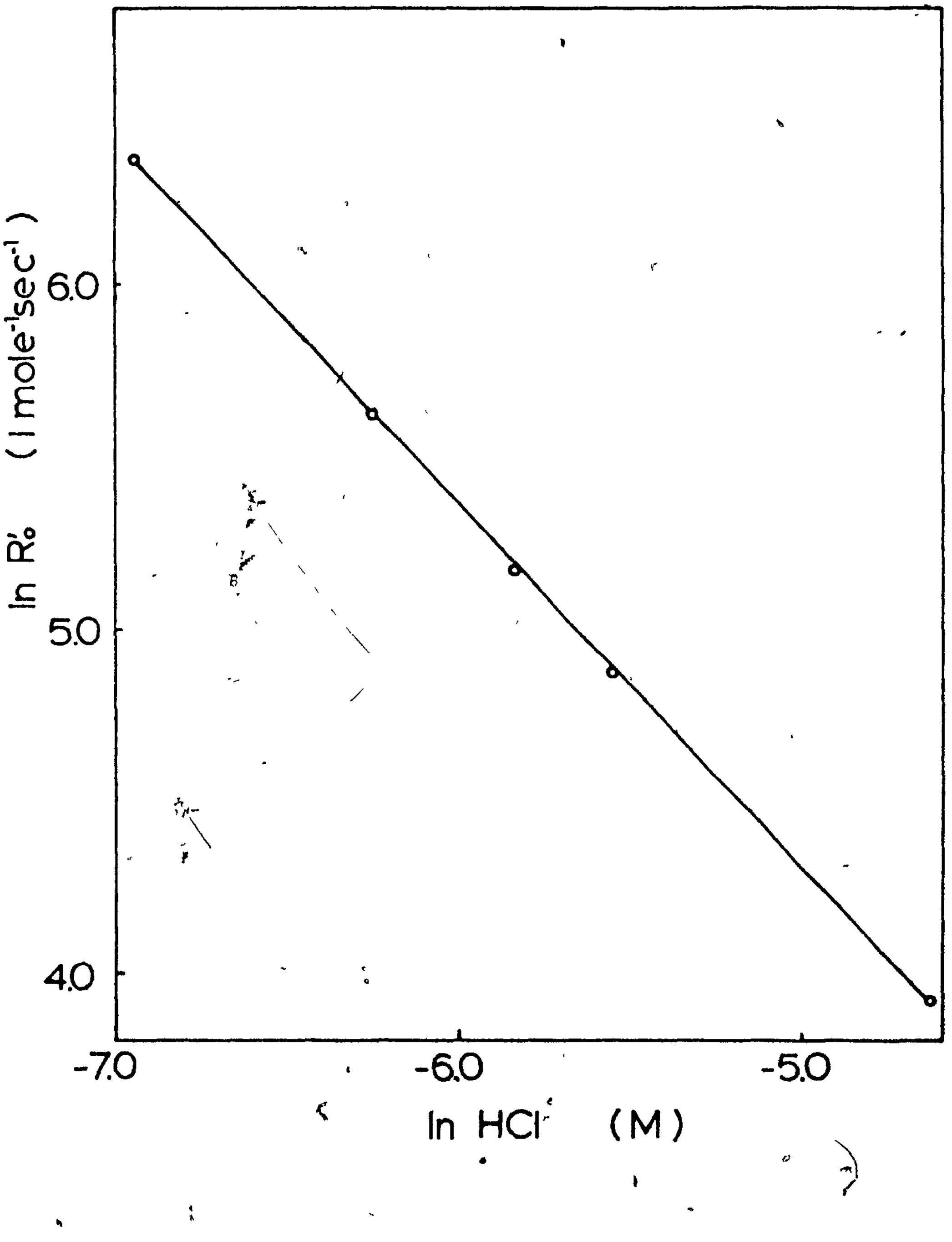
TABLE 3

DEPENDENCE OF THE INITIAL RATE OF HYDROLYSIS OF FORMAMIDINEDISULFIDE UPON HYDROCHLORIC ACID CONCENTRATION AT 25°C, FOR INITIAL CONCENTRATION OF DISULFIDE OF 2.3×10^{-4} M

D_o (M)	HCl (M)	R_o ($M^{-1}cm^{-1}min^{-1}$)	$R_o/D_o = R'_o$
0.0002347	0.000965	0.136	579
0.0002333	0.001930	0.0645	276
0.0002401	0.000290	0.0421	175
0.0002392	0.00386	0.0313	131
0.0002409	0.00965	0.0121	50.2

FIGURE 10

VARIATION OF INITIAL RATE OF CHANGE OF ABSORBANCE AT 236 nm WITH INITIAL CONCENTRATION OF HYDROCHLORIC ACID



ln R'₀ (l mole⁻¹sec⁻¹)
6.0
5.0
4.0
-7.0
-6.0
-5.0
ln HCl (M)

$$\frac{d[Tu]_t}{dt} = 3\,k'K_w\,[D][OH^-] = \frac{1}{10800}\,\frac{dA_{236}}{dt} \qquad (48)$$

Using the experimental data in Tables 2 and 3 and $K_w = 1.008 \times 10^{-14}$, a value is obtained for $k'K_w^{-1}$ of $(2.74 \pm 0.16) \times 10^{+7}\,M^{-1}sec^{-1}$ at 25°C.

In Table 4 (Figure 11) are recorded values of the rate constant $k_T = 3k'K_w^{-1}$ over the temperature range 20.0 to 40.0°C. These give an apparent activation energy for the rate-determining step of 7.8 kcal $mole^{-1}$. The corresponding change in the free energy of activation with temperature, given by $\Delta G^{\ddagger} = -RT \ln k_T \frac{h}{kT}$ yields an entropy of activation for the rate determining step of $\Delta S^{\ddagger} = -2$ e.u., (Table 5, Figure 12).

HYDROLYSIS OF THE FULLY N-METHYLATED FORMAMIDINE-DISULFIDE IN DILUTE ACID, pH $\leq$ 4

The surprising ease with which formamidinedisulfide was hydrolyzed suggested that similar studies be made with the fully N-methylated disulfide. Accordingly, 1,1,3,3-tetramethyl-2-thiourea (TMT) was oxidized to the diperchlorate salt of di-(tetramethylformamidine)disulfide (TMD) (mp 232-235°C, decomposition at 255°C) by the method of Lecher et al (86). Analyses of the disulfide agreed with the formula for an anhydrous diperchlorate salt. The UV spectrum of

TABLE 4

VARIATION OF THE OBSERVED RATE CONSTANT FOR THE HYDROLYSIS OF FORMAMIDINEDISULFIDE IN HCl SOLUTION WITH TEMPERATURE

$T^{o}K$	$k_T = 3\ k'\ K_w^{-1}$ * $M^{-1}sec^{-1}$
293.2	$(6.00 \pm 0.08) \times 10^7$
298.2	$(8.23 \pm 0.50) \times 10^7$
303.2	$(8.99 \pm 0.14) \times 10^7$
308.2	$(14.5 \pm 0.2) \times 10^7$
313.2	$(14.5 \pm 0.2) \times 10^7$

* Values for k_T are the averages of at least three determinations at each temperature.

FIGURE 11

ARRHENIUS PLOT OF THE RATE CONSTANT FOR HYDROLYSIS OF FORMAMIDINIUMDISULFIDE OVER THE TEMPERATURE RANGE 20.0 TO 40.0°C.

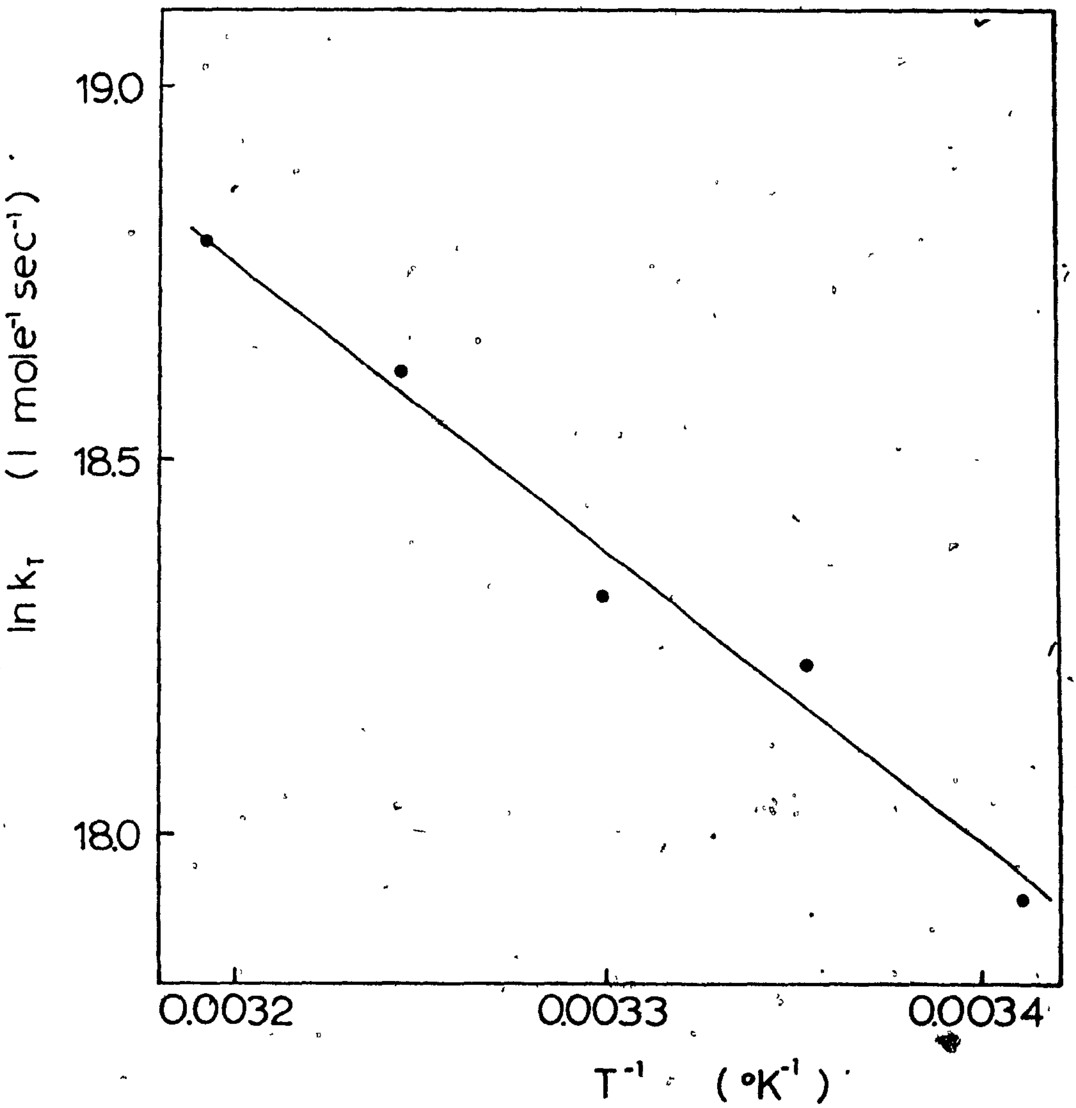

19.0
18.5
18.0
ln k$_T$ (l mole^{-1} sec^{-1})
0.0032
0.0033
0.0034
T^{-1} (°K^{-1})

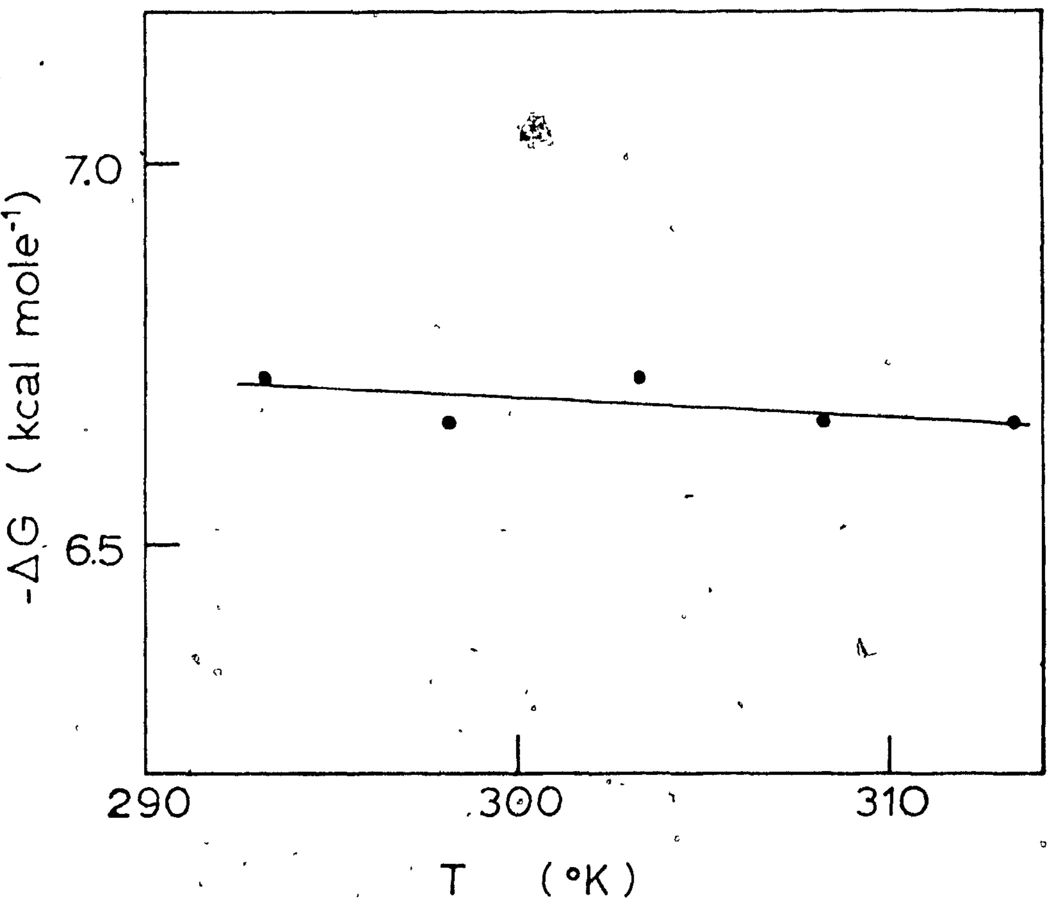
TABLE 5

VARIATION OF THE FREE ENERGY OF ACTIVATION FOR THE HYDROLYSIS OF FORMAMIDINE DISULFIDE IN HCl SOLUTION WITH TEMPERATURE

T °K	k_T ($M^{-1}sec^{-1}$)	$-\Delta G^{\ddagger}$ ($kcal\ mole^{-1}$)
293.2	(6.00±0.008) x 10^7	6.72
298.2	(8.23±0.50) x 10^7	6.66
303.2	(8.99±0.14) x 10^7	6.72
308.2	(12.2±0.2) x 10^7	6.66
313.2	(14.5±0.2) x 10^7	6.66

FIGURE 12

VARIATION OF FREE ENERGY OF ACTIVATION FOR THE HYDROLYSIS OF FORMAMIDINIUMDISULFIDE OVER THE TEMPERATURE RANGE 20.0 TO 40.0°C


7.0
6.5
-ΔG (kcal mole-1)
290
300
310
T (°K)

tetramethylthiourea and the infrared and UV spectra of its disulfide diperchlorate were recorded (Figures 13-15).

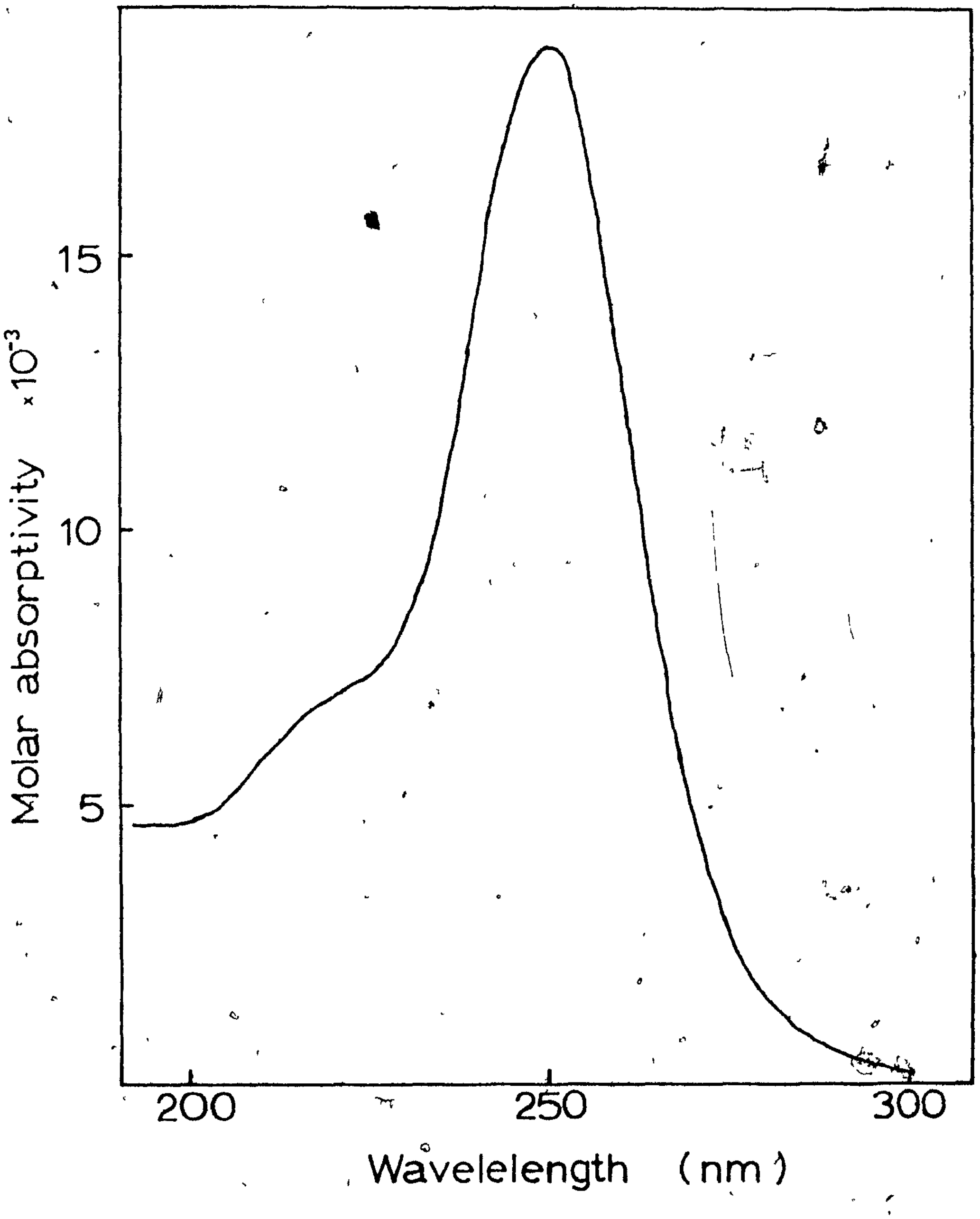
When the di-(tetramethylformamidine)disulfide diperchlorate salt was dissolved in distilled water ($pH^{o} \simeq 7$) there was an instantaneous drop in pH to a value of approximately 2-3. When the salt was dissolved in dilute HCl ($pH^{o}=2.63$ at 25°C) a more gradual pH drop was obtained (Figure 16). The acidity released during hydrolysis of the disulfide was titrated with standard sodium hydroxide solution and found to correspond to two equivalents of acid per mole of the disulfide decomposed. No sulfur was formed during the titration with hydroxide, in contrast to the corresponding titration of formamidinedisulfide.

The changes in the UV spectrum when the di-(tetramethylformamidine) disulfide diperchlorate was dissolved in dilute HCl(0.0005 to 0.05 M) corresponded to the formation of tetramethylthiourea (Figure 17). The absorbance at 249 nm after hydrolysis was complete corresponded to ~ 1.45 moles of tetramethylthiourea per mole of disulfide hydrolyzed.

On the basis of the final absorbance at 249 nm for the hydrolysis of di-(tetramethylformamidine)disulfide it may be assumed that the tetramethylformamidine sulfinic acid (TMS) formed in the hydrolysis possesses negligible absorbance at this wavelength compared with that of tetramethylthiourea. With this assumption, Eqn. (38) may be applied to the hydrolysis

FIGURE 13

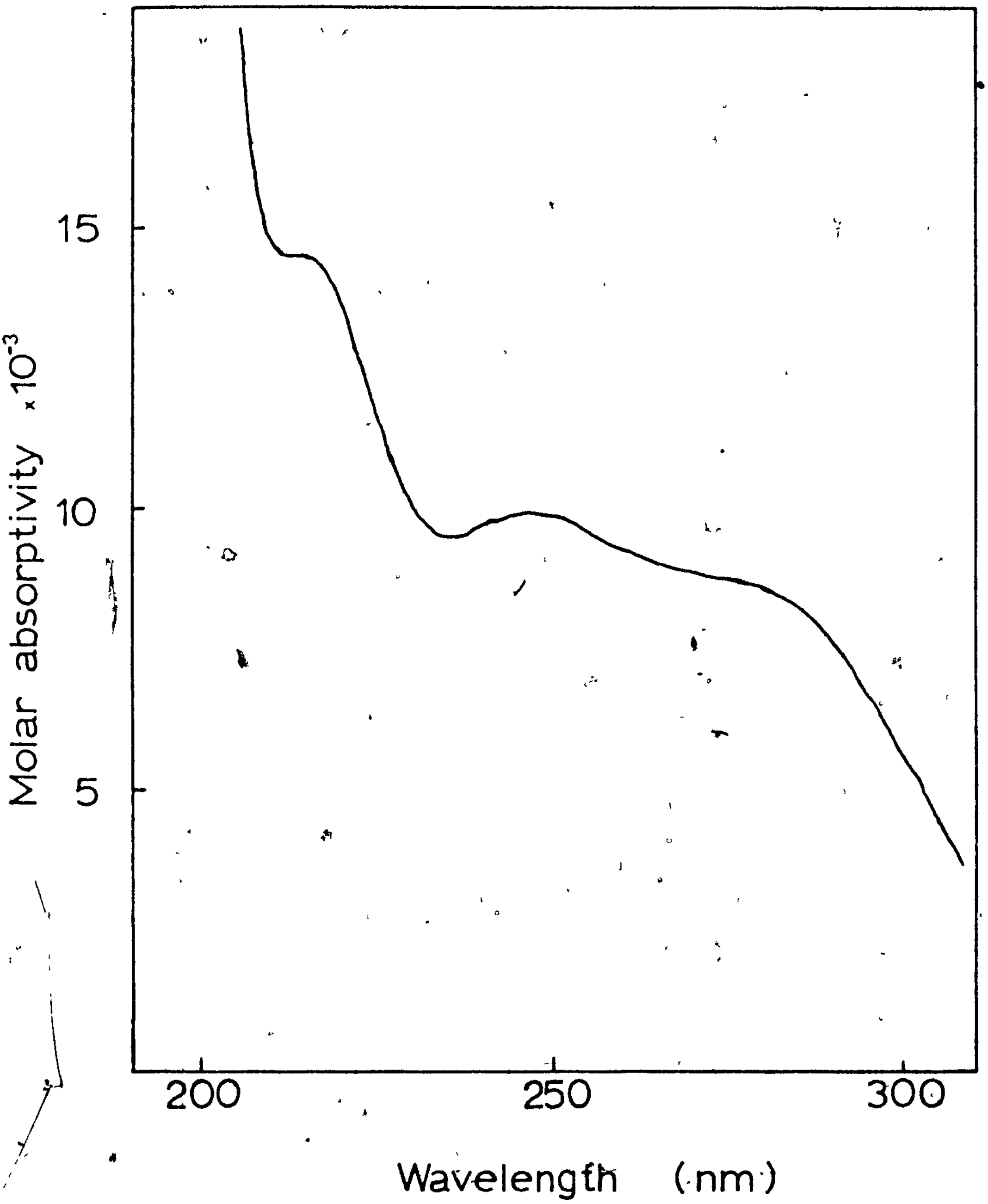
UV ABSORPTION SPECTRUM OF 1,1,3,3-TETRAMETHYL-2-THIOUREA IN AQUEOUS SOLUTION AT pH = 7



15
10
5
Molar absorptivity ×10⁻³
200
250
300
Wavelelength (nm)

FIGURE 14

UV ABSORPTION SPECTRUM OF DI-(TETRAMETHYLFORMAMIDINIUM)DISULFIDE IN 0.4 M HCl



Molar absorptivity ×10⁻³
15
10
5
200
250
300
Wavelength (nm)

FIGURE 15

INFRARED ABSORPTION SPECTRUM OF DI-(TETRAMETHYLFORMAMIDINIUM) DISULFIDE DIPERCHLORATE AS NUJOL MULL

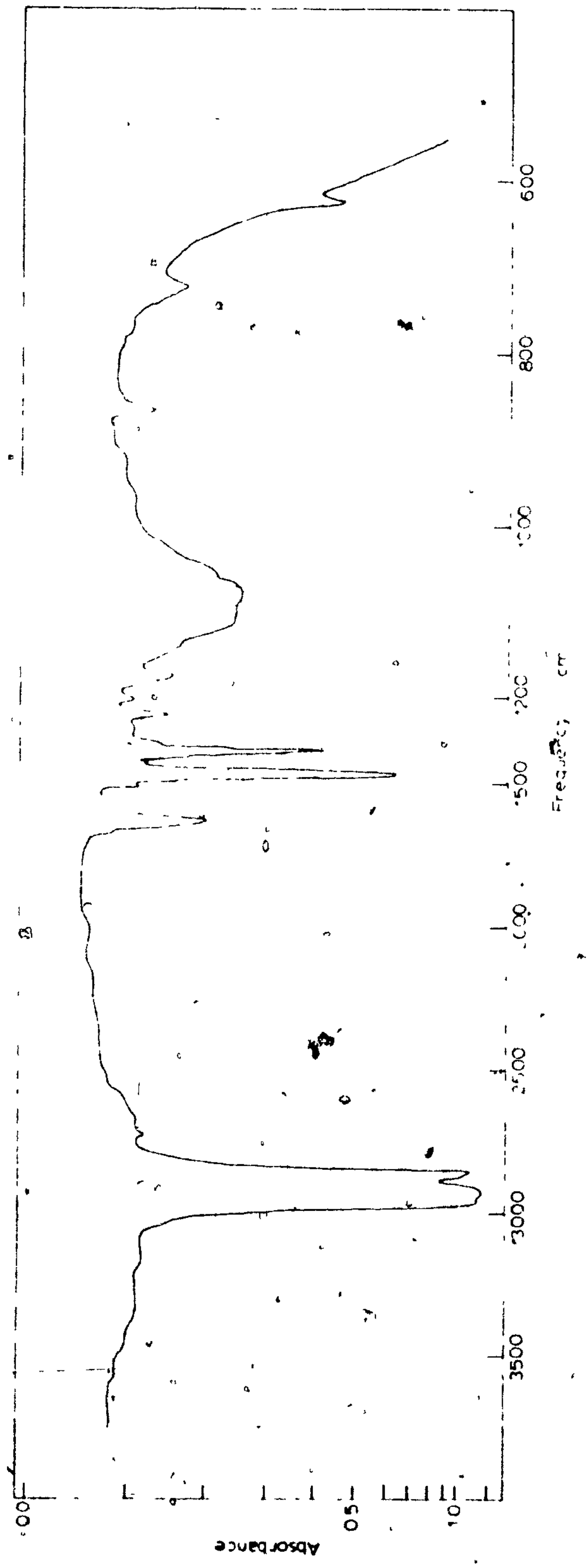

Absorbance
0.0
0.5
1.0
3500
3000
2500
2000
1500
1200
1000
800
600
Frequency cm⁻¹

FIGURE 16

DECREASE IN pH CAUSED BY HYDROLYSIS OF DI-(TETRAMETHYLFORMAMIDINIUM)DISULFIDE DIPERCHLORATE IN DILUTE HYDROCHLORIC ACID WITH AN INITIAL pH OF 2.63

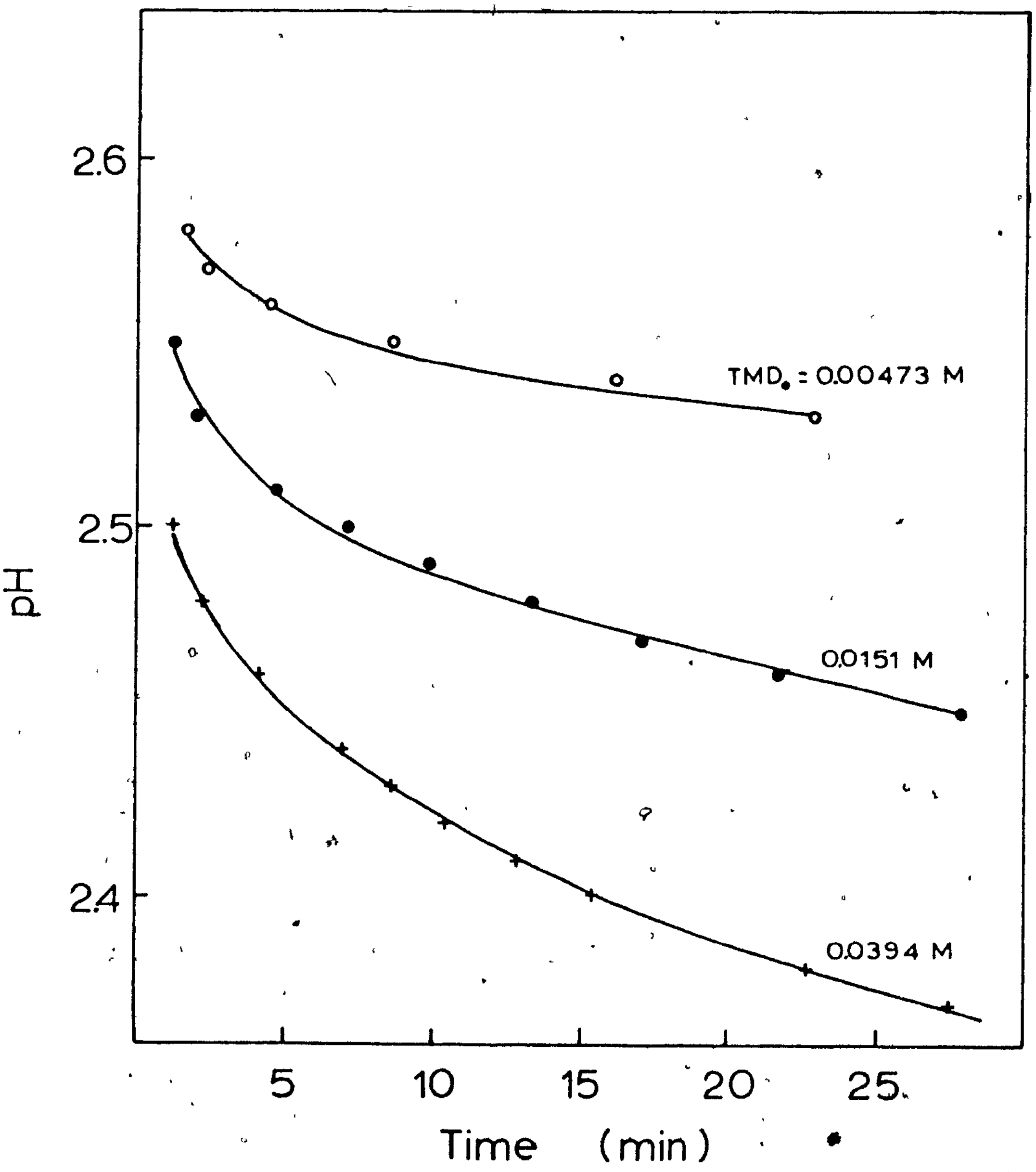
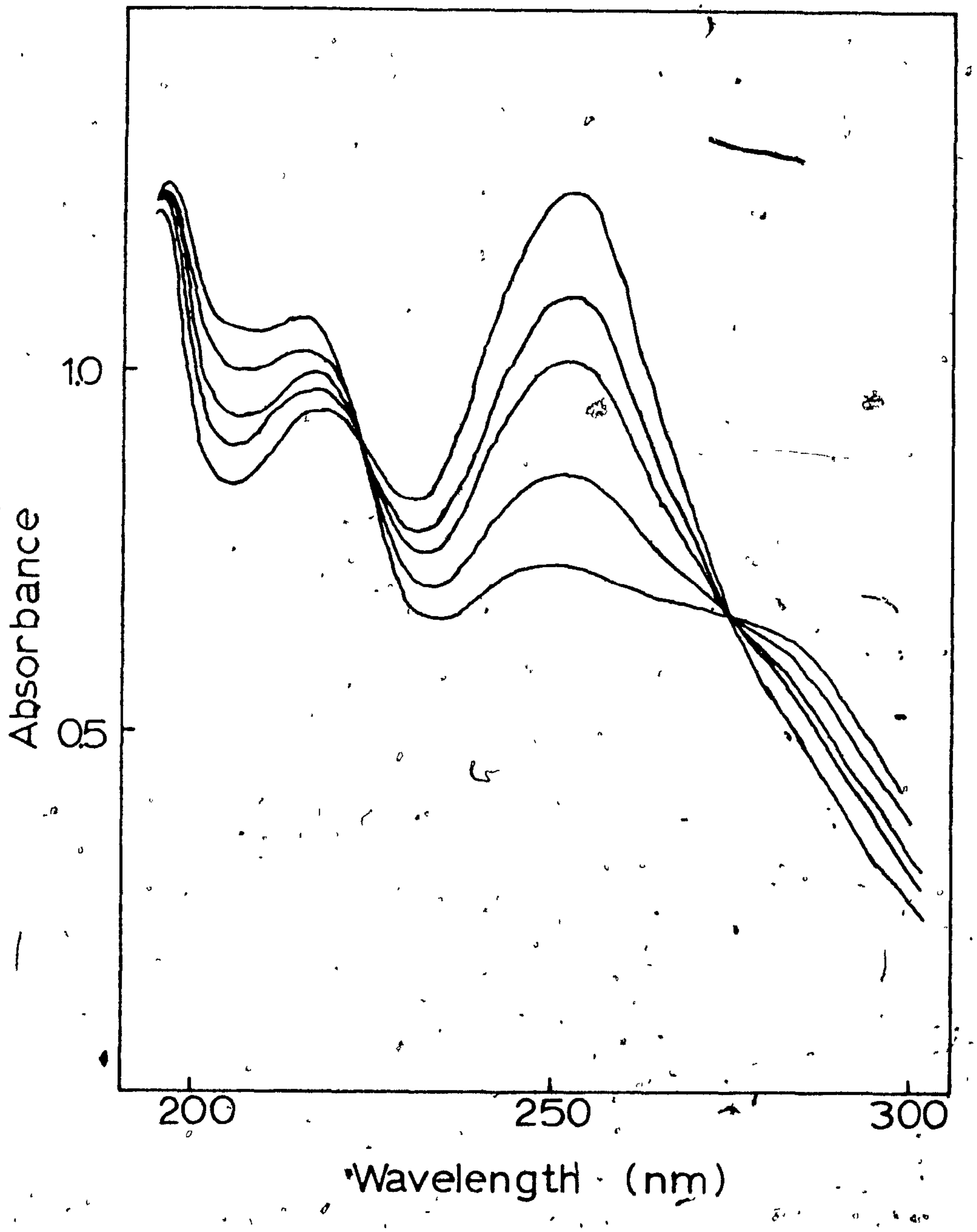

2.6
2.5
2.4
pH
TMD$_o$ = 0.00473 M
0.0151 M
0.0394 M
5
10
15
20
25
Time (min)

FIGURE 17

INCREASE OF THE UV ABSORPTION AT 249 nm OF A DILUTE ACID SOLUTION OF DI-(TETRAMETHYLFORMAMIDINE)DISULFIDE DIPERCHLORATE DUE TO HYDROLYSIS



Absorbance
1.0
0.5
200
250
300
Wavelength (nm)

of di(tetramethylformamidine)disulfide diperchlorate with appropriate values for molar absorptivities and concentrations, to yield

$$\frac{dA_{249}}{dt} = 9946\ \frac{d[\mathrm{TMD}]_t}{dt} + 18860\ \frac{d[\mathrm{TMT}]_t}{dt} = \dot{R}_o \qquad (49)$$

where TMD and TMT denote di-(tetramethylformamidinium) disulfide diperchlorate and tetramethylthiourea, respectively.

The rate of the hydrolysis reaction is defined by

$$r = -\frac{1}{2}\frac{d[\mathrm{TMD}]}{dt} = \frac{1}{3}\frac{d[\mathrm{TMT}]}{dt} = \frac{d[\mathrm{TMS}]}{dt} = \qquad (50)$$

$$= k_1\ [\mathrm{TMD}]^m\ [\mathrm{HCl}]^n$$

and from Eqn. (49).

$$\frac{dA_{249}}{dt} = 12200\ \frac{d\ \mathrm{TMT}}{dt} = 3 \times 12200\ k_1[\mathrm{TMD}]^m[\mathrm{HCl}]^n \qquad (51)$$

Thus, the order of the reaction in disulfide and acid can again be determined by measuring the initial rates at which the absorbance at 249 nm changes for different concentrations of the disulfide and acid. With the Perkin-Elmer 402 UV-visible spectrophotometer in the time-drive mode, these initial rates were recorded at 20°C for di-(tetramethylformamidine)disulfide diperchlorate in HCl of 5.00×10^{-3} M concentration for initial disulfide concentrations over the range 1.36×10^{-5} to 1.32×10^{-4} M (Table 6). The least-mean-squares slope of a plot of ln R_o against ln TMD_o (Figure 18) was found to be + 0.95, which indicates that the rate of alkaline hydrolysis of di-(tetramethylformamidine)disulfide diperchlorate is first order in disulfide at constant pH, i.e. m=1 in Eqn. (49).

Similar studies with a disulfide concentration of ca. 0.000044 M, over a range of acid concentrations from 5.00×10^{-4} to 5.00×10^{-3} M and with a disulfide concentration of 0.00013 M over the range of acid concentration from 5.00×10^{-3} to 15.0×10^{-3} M (Table 7), gave a plot of ln R_o against ln HCl_o with a slope of -1.0 (Figure 19). It may be inferred, therefore, that the reaction is also first-order in hydroxide ion.

From the experimental data in Tables 6 and 7, with $K_W = 0.681 \times 10^{-14}$ at 20°C, a value is obtained for $k = (11.6 \pm 0.8) \times 10^{7}\ M^{-1} sec^{-1}$

Table 8 (Figure 20) shows values of the rate constant $k_T = 3k\, K_W^{-1}$, over the temperature range 20.0 to 40.0°C. From these data the apparent activation energy is 1.8 kcal $mole^{-1}$ for the rate determining step. The corresponding change in the free energy of activation with temperature yields an entropy of activation of $\Delta S^{\ddagger} = + 16$ e.u. (Table 9, Figure 21).

TABLE 6

DEPENDENCE OF THE INITIAL RATE OF HYDROLYSIS ON THE INITIAL DISULFIDE CONCENTRATION AT 20.0°C IN HCl OF 5.00 x 10^{-3} M CONCENTRATION

TMD_o (M)	R_o (min^{-1})
0.0000136	0.00483
0.0000298	0.00950
0.0000466	0.0161
0.0000654	0.0214
0.0000915	0.0295
0.000111	0.0325
0.000132	0.0437

FIGURE 18

VARIATION OF INITIAL RATE OF CHANGE OF ABSORBANCE AT 249 nm WITH INITIAL CONCENTRATION OF TMD IN 0.005 M HCl AT 20.0°C

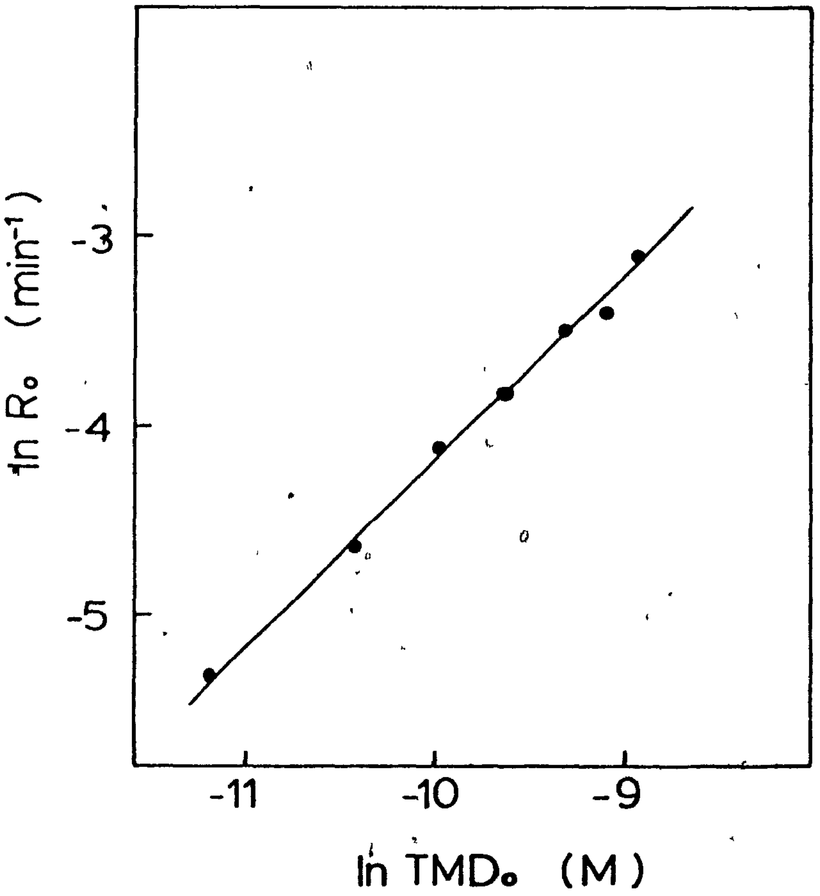

ln R₀ (min⁻¹)
-3
-4
-5
-11
-10
-9
ln TMD₀ (M)

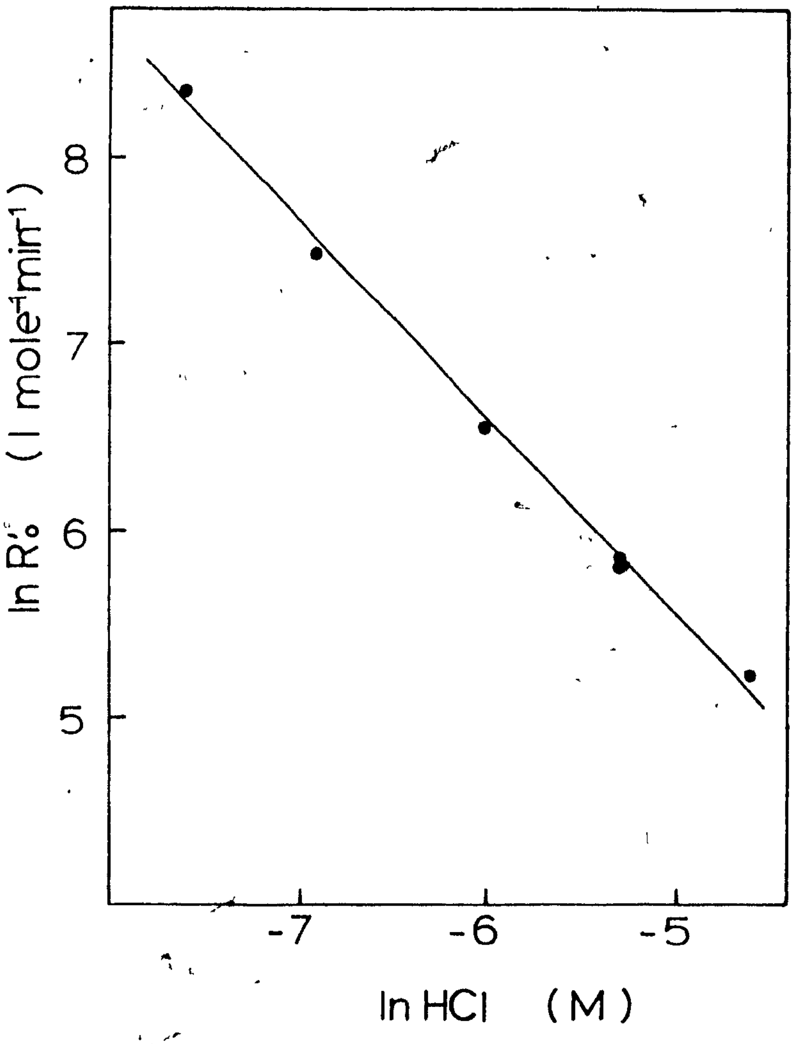
TABLE 7

DEPENDENCE OF INITIAL RATE OF HYDROLYSIS OF DITETRAMETHYLFORMAMIDINEDISULFIDE DIPERCHLORATE UPON HYDROCHLORIC ACID CONCENTRATION AT 20.0°C FOR INITIAL CONCENTRATIONS OF DISULFIDE OF 4.4 x 10^{-5} AND 1.3 x 10^{-4} M

TMD_o (M)	HCl (M)	R_o (min^{-1})	$\ln \frac{R_o}{TMD_o}$ = $\ln R'_o$
0.0000440	0.000500	0.188	8.35
0.0000438	0.00100	0.0774	7.47
0.0000468	0.00248	0.0329	6.55
0.0000466	0.00500	0.0161	5.84
0.0001316	0.00500	0.0437	5.80
0.0001291	0.0100	0.0243	5.23
0.0001308	0.0150	0.0204	5.05

FIGURE 19

VARIATION OF INITIAL RATE OF CHANGE OF ABSORBANCE AT 249 nm WITH INITIAL CONCENTRATION OF HCl AND 0.000044 M TMD_o AT 20.0° C



8
7
6
5
ln R$_0^c$ (l mole^{-1}min^{-1})
-7
-6
-5
ln HCl (M)

TABLE 8

VARIATION OF THE OBSERVED RATE CONSTANT FOR THE HYDROLYSIS OF DI-TETRAMETHYLFORMAMIDINEDISULFIDE DIPERCHLORATE IN HCl SOLUTION WITH TEMPERATURE

T °K	$k_T = 3k_1K_W^{-1}$ $M^{-1}sec^{-1}$
293.2	$(34.7 \pm 1.5) \times 10^7$
298.2	$(39.3 \pm 1.4) \times 10^7$
303.2	$(41.1 \pm 1.8) \times 10^7$
308.2	$(42.2 \pm 1.6) \times 10^7$
313.2	$(43.5 \pm 1.8) \times 10^7$

FIGURE 20

ARRHENIUS PLOT OF THE RATE CONSTANT FOR THE HYDROLYSIS OF TMD OVER THE TEMPERATURE RANGE 20.0 TO 40.0^{o} C.

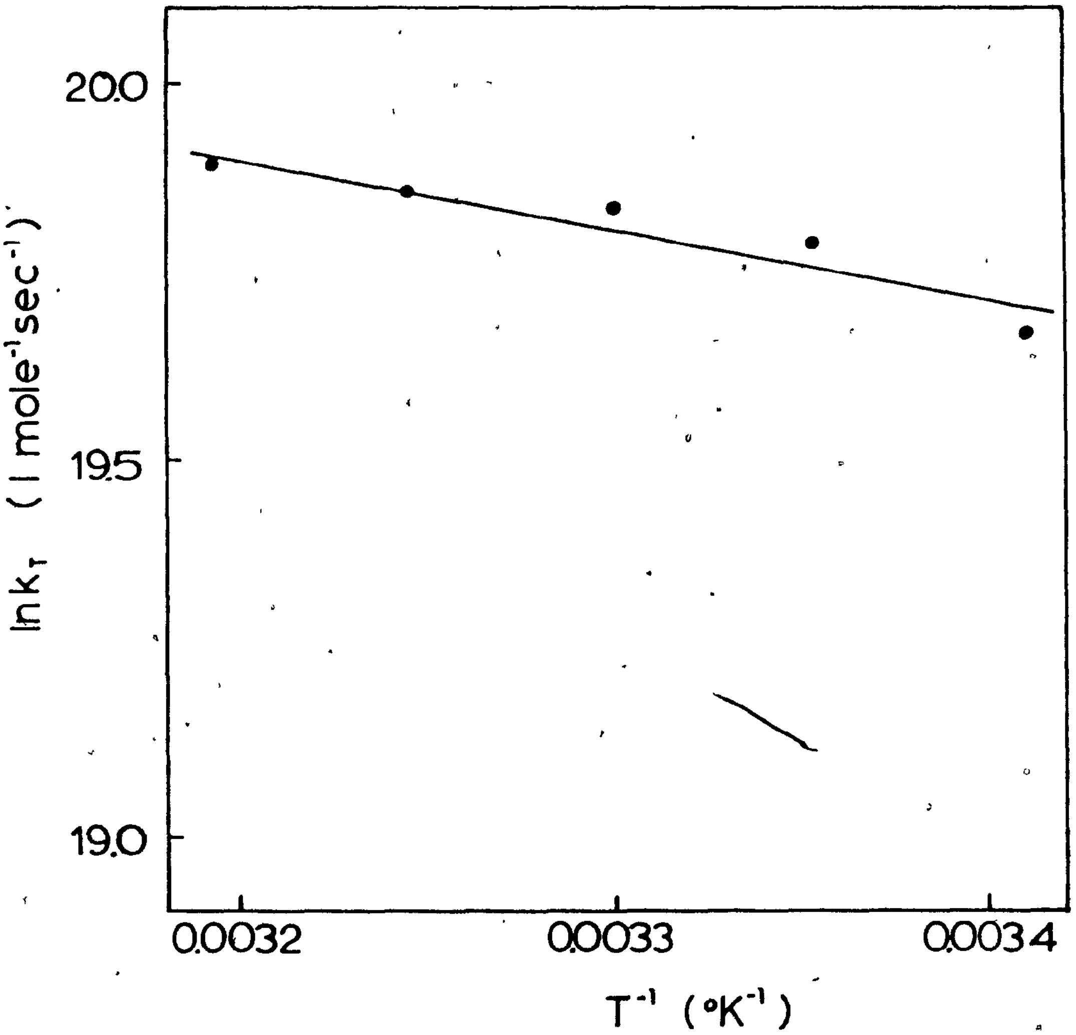

20.0
19.5
19.0
0.0032
0.0033
0.0034
$\ln k_T$ (l mole^{-1}sec^{-1})
T^{-1} (°K^{-1})

TABLE 9

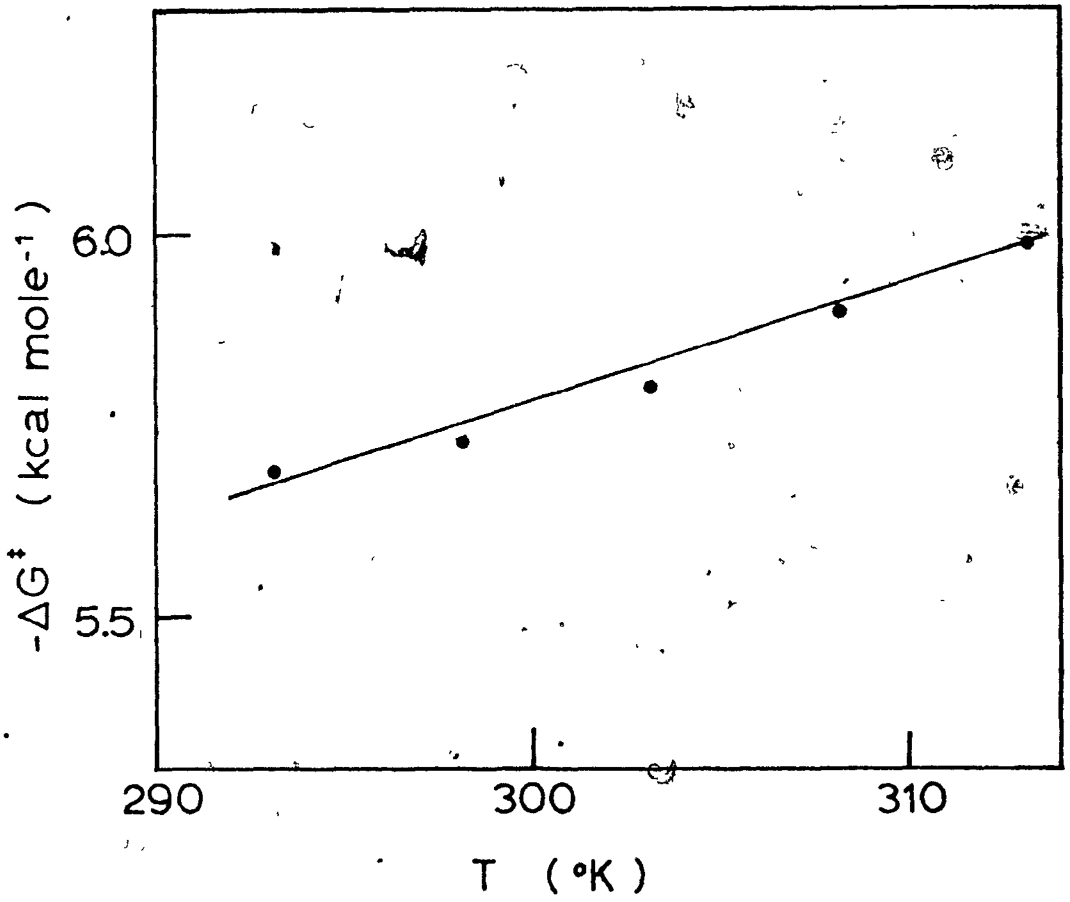
VARIATION OF THE FREE ENERGY OF ACTIVATION FOR THE HYDROLYSIS OF DI-TETRAMETHYLFORMAMIDINE DISULFIDE IN HCl SOLUTION WITH TEMPERATURE

T °K	k_T $M^{-1}sec^{-1}$	$-\Delta G^{\ddagger}$ kcal $mole^{-1}$
293.2	$(34.7 \pm 1.5) \times 10^7$	5.69
298.2	$(39.3 \pm 1.4) \times 10^7$	5.73
303.2	$(41.1 \pm 1.8) \times 10^7$	5.80
308.2	$(42.0 \pm 1.6) \times 10^7$	[illegible].90
313.2	$(43.5 \pm 1.8) \times 10^7$	5.99

FIGURE 21

VARIATION OF FREE ENERGY OF ACTIVATION FOR THE HYDROLYSIS OF TMD IN HCl SOLUTION WITH TEMPERATURE

6


-ΔG‡ (kcal mole-1)
6.0
5.5
290
300
310
T (°K)

It is interesting to note that acidification of the alkaline (pH = 9-10) solution containing the hydrolysis products of di-(tetramethylformamidine)disulfide renders it capable of oxidizing thiourea to formamidinedisulfide and iodide to iodine (87). This indicates the formation of an oxidizing agent with reasonable stability, presumably tetramethylformamidinesulfinic acid.

DISCUSSION

Three possible mechanisms have been demonstrated experimentally for the alkaline hydrolysis of organic disulfides. These involve α-elimination (88,89), β-elimination (83), or direct nucleophilic displacement of sulfur from sulfur by hydroxide ion (83,84,90). The mode of hydrolysis for a given disulfide apparently depends on secondary features of its molecular structure (91).

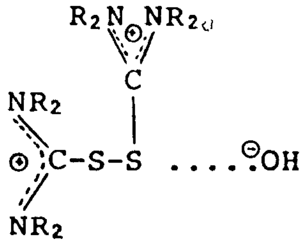
Although formamidinesulfinic acid could not be isolated in the hydrolysis of formamidinedisulfide, the relatively high yield of thiourea obtained indicates that the hydrolysis in dilute acid involves direct attack of hydroxide ion upon the disulfide bond. An alternative mechanism that would give rise to 1.4 moles of thiourea per mole of disulfide does not appear likely.

It has been shown that a negative charge on the disulfide, not far removed from one of the sulfur atoms, inhibits direct nucleophilic attack of hydroxide on the disulfide bond, whereas it is considerably accelerated by a positive charge on a disulfide (83). This suggests that formamidinedisulfides, with positive charges directly adjacent to the disulfide bond, should be much more reactive than neutral alkyl or aryldisulfides. The inductive effect of the methyl groups in di-(tetramethylformamidine)disulfide could not greatly reduce the activating effect of the positive charges.

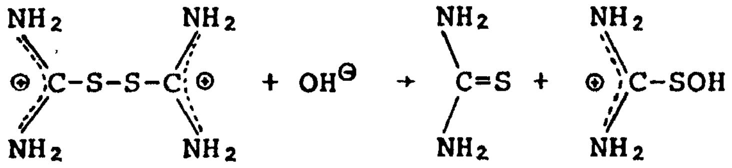
Since steric effects in the methylated disulfide do not seem to affect its reactivity with thiourea, neither should they decrease its reactivity to hydroxide.

Danehy and Parameswaran (92) have shown that for aromatic disulfides the rate of hydrolysis increases with decreasing pK of the displaced thiol. Thus, $(p\text{-}{}^{-}\text{OOCC}_6\text{H}_4\text{S-})_2$, with a thiol pK of 5.85, has a half-life of 7 minutes in 0.125 N NaOH, whereas, the half-life of $(o\text{-MeC}_6\text{H}_4\text{S-})_2$ with a pK of 6.64, is increased to 24 hours under the same conditions. Protonated thioureas have pK_a values in the range -1 to -2 (93,94), indicating that thioureas should be very good leaving groups in nucleophilic displacement reactions. Tetramethylthiourea has a lower pK_a than thiourea itself, so that the former presents a better leaving group in a nucleophilic displacement reaction. The observed higher rate of hydrolysis of the di-(tetramethylformamidine)disulfide may be taken to mean that steric and inductive effects on the disulfide reactivity are less important than the pK_a of the leaving group.

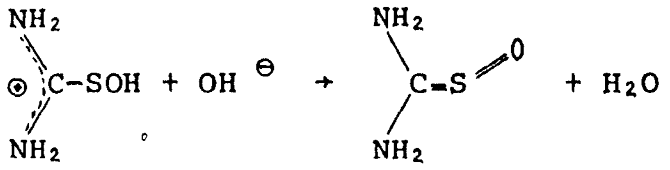
The great importance that the pK_a of the leaving group exercises in determining the rate of hydrolysis may be interpreted in terms of a rate determining sulfur-sulfur bond cleavage in the transition complex



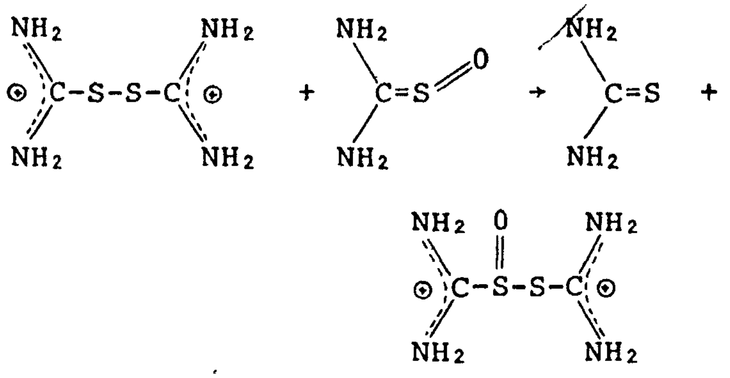
While direct nucleophilic displacement at sulfur is the only possible mode of decomposition for di-(tetramethylformamidine)disulfide, the unsubstituted formamidinedisulfide may undergo alkaline hydrolysis by two possible mechanisms. In acid solutions (pH ≤ 4) the hydrolysis apparently proceeds by hydroxide attack at the disulfide bond, to form thiourea and eventually formamidinesulfinic acid which then slowly decomposes.



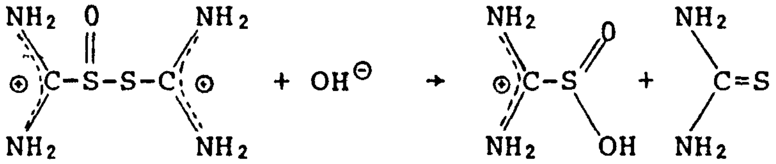
(52)



(53)

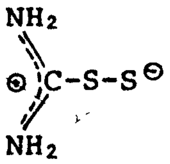


(54)

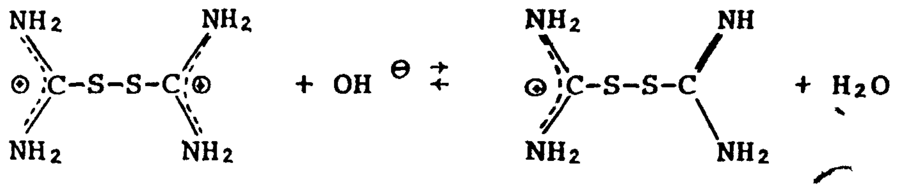


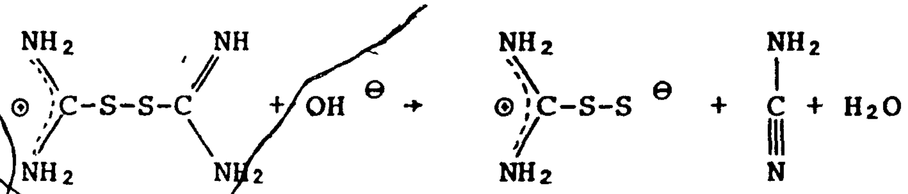
(55)

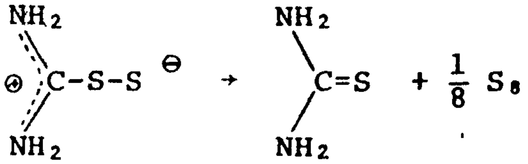
On the other hand, the alkaline hydrolysis at pH > 5 appears to be more complicated, and it is suggested that it might involve displacement of the unfavorable leaving group



by a sequence such as


(56)


(57)


(58)

The observed formation of hydrogen sulfide in strong base is not explicable at present, and the reaction under these conditions is so fast that no kinetic studies have been attempted to elucidate the reaction mechanism.

THIOUREA COMPLEXES WITH COPPER SALTS

INTRODUCTION

Numerous investigations have been made of thiourea as a levelling and brightening agent during the electroplating of copper from acid copper sulfate baths. Little attention has been given, however, to the reaction of thiourea with cupric sulfate, which ultimately produces formamidinedisulfide and cuprous-thiourea complexes. (95).

Complexes of thiourea with cuprous salts by reaction of excess thiourea with the corresponding cupric salts were first prepared and characterized in 1880 (96). Rathke (52) obtained the first reliable analyses and gave very thorough descriptions of many cuprous thiourea salts. His formula for pentathioureadicuprous sulfate dihydrate as the complex with cuprous sulfate was later confirmed by other workers(97,98).

Walter, Storfer and their associates (72,73,99-102) claimed to find pentathioureadicuprous sulfate monohydrate as the only thiourea complex with cuprous sulfate, but Nardelli and his co-workers subsequently proposed that the salt was a trihydrate (103). They also described the preparation of a hexathioureadicuprous sulfate dihydrate (103).

It has been demonstrated (76) that the concentrated aqueous solutions of cuprous-thiourea salts contain complex species such as $[Cu_2Tu_5.H_2O]^{2+}$ and $[Cu_2Tu_6H_2O]^{2+}$ whereas in the presence of excess thiourea $[CuTu_4]^+$ is the predominant species (74,75).

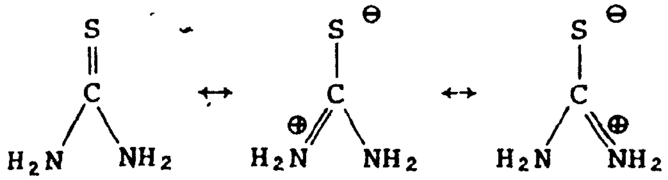
The formation of a white precipitate has been observed near the cathode (28) during electrolysis in acid copper sulfate baths containing thiourea, and small amounts of a highly insoluble, colorless complex containing cuprous ions and thiourea have been isolated. (38) However, no formula could be derived for the complex from its elemental analyses.

In solutions of thiourea in acid copper sulfate, Hintermann and Javet (40) found a UV absorption band which was not present in either of the constituents alone. On the basis of available information, they assumed this band to be due to a cuprous-thiourea complex without considering the possibility that it might be associated with a cupric-thiourea species. It was argued that the necessary cuprous ions were formed by reduction of cupric ions, with concomitant formation of formamidinedisulfide.

Application of Job's method of continuous variation (104) to mixtures of cuprous ions (method of preparation unspecified) and thiourea apparently showed the new band at 340 nm to be due to a cuprous-thiourea complex, $Cu^{+}.SCN_2H_4$, with a maximum molar absorptivity of $\varepsilon_{340} = 10^3$ (105). This molar absorptivity value, together with the data given by Job's method, permits calculation of apparent association constants of 8.33, 7.75 and 2.35 for $[Cu^{+}] = [Tu]$ of 0.0025, 0.0050 and 0.025 M respectively. These values are to be compared with an average association constant of $\overline{K} \approx 10^4$ calculated from polarographic data (74,75).

No attempt was made to elucidate the electronic origin of the absorption band, but it was speculated that a symmetry-forbidden electronic transition in thiourea was allowed in the cuprous-thiourea complex, due to a symmetry lowering from C_{2v} to C_s.

For some time, the mode of coordination in metal-thiourea complexes was considered open to debate and infra red spectra were sometimes interpreted in terms of nitrogen coordination. However, coordination through sulfur is favoured by data from dipole moment (106), dielectric constant (107,108), and diamagnetic susceptibility measurements (109), which indicate considerable charge separation in the thiourea molecule due to ionic resonance forms, with a resonance energy of 27 kcal mole^{-1} (110),



This view has also found strong support in x-ray structure determinations of many metal-thiourea complexes(111-119) which all contain sulfur coordinated thiourea as ligand. It is a reasonable assumption, therefore, that any thiourea complexes with copper will contain sulfur coordinated thiourea as ligand. In view of this, the effect of protonation on the π electron distribution and symmetry of thiourea should be very similar to formation of complexes with cuprous ions and should give rise to similar changes in the electronic absorption spectrum (120). However, protonation causes disappearance of the thiourea band at 236 nm and does not result in the formation of new absorption bands in the region 300-400 nm (121).

Javet and Hintermann demonstrated that sulfur was the site of coordination by the observation that all N-methylthioureas gave rise to maxima in the 340-370 nm region (37), whereas, no such band was present when S-methylisothiourea derivatives were added to the plating bath.

The preparation of cupric thiourea complexes has recently been reported, which renders untenable the belief that such complexes are not capable of existence (74). In these mixed complexes of π-acceptor ligands and thiourea with copper II, the stabilization of the cupric state is probably due to the strong chelating ability of the ligands with π bonding from metal to ligand which produces some electron delocalization in the chelate ring (119,122). Dichlorobis-(tetramethylthiourea) copper (II) has also been prepared, but no reason was advanced for its stability (118).

EXPERIMENTAL AND RESULTS

Equipment

Spectra were recorded on a Perkin-Elmer 402 UV-visible spectrophotometer fitted with a thermostatted cell holder.

Analyses for C, N, and H were made with a Hewlett-Packard 185 CHN-analyzer, while cupric ion was determined by EDTA titration with murexide as indicator.

Potential and pH measurements were made relative to a saturated calomel reference electrode, using an Orion model 701 digital millivolt/pH meter. An Orion model 94-29 cupric ion electrode was used for the measurement of cupric ion activity.

Materials

Water used in preparing all solutions was deionized and distilled. Thiourea (Baker analyzed reagent) and tetramethylthiourea (Eastman) were used without further purification. Sulfuric acid (Anachemia, reagent grade, 96%) was used as supplied, but cupric sulfate pentahydrate (Fisher certified reagent) was once recrystallized from acidified distilled water to minimize insoluble impurities.

PREPARATION OF TRITHIOUREADICUPROUS SULFATE MONOHYDRATE

When thiourea (0.003 to 0.08 M) was dissolved in the acid copper sulfate electroplating bath (0.50 M $CuSO_4$, 1.00 M H_2SO_4), a green color appeared, which faded during a period (one to several hours) that depended on the concentration of thiourea used. A precipitate of white, microscopic needles was obtained as the product of this reaction. This compound was found to contain cuprous copper, thiourea and sulfate ions, but the copper content (approximately 26%) indicated that it was not the pentathioureadicuprous sulfate dihydrate described in the literature (19.83% Cu). Several samples of the white needles were prepared in a nitrogen atmosphere for a range of thiourea concentrations in 0.5 M $CuSO_4$ 1.0 M H_2SO_4 (Table 10). At concentrations of thiourea below 0.01 M no solid complex was formed within 24 hours, although small amounts were precipitated after approximately 72 hours. However, when metallic copper was immersed in these solutions, the formation of white needles was observed on the surface of the copper after a few hours. The same analyses were obtained for the complex formed in the presence and in the absence of metallic copper (Table 11). The analyses would seem to correspond to trithioureadicuprous sulfate monohydrate, $Cu_2Tu_3SO_4H_2O$, in accordance with the observation that in the concentration range 0.05 to 0.10 M thiourea, the yield of complex approaches that expected for monohydrate formation by the reaction

TABLE 10

YIELD OF $Cu_2Tu_3SO_4H_2O$ AFTER 24 HOURS AS A FUNCTION OF INITIAL THIOUREA CONCENTRATION IN 0.5 M $CuSO_4$, 1.0 M H_2SO_4 AT 25°C UNDER N_2

$[\text{Thiourea}]_o$ M	wt $Cu_2Tu_3SO_4H_2O$ g	% yield of Tu as $Cu_2Tu_3SO_4H_2O$
0.0763	5.1795	51.0
0.0443	2.6846	45.5
0.0254	1.2346	36.6
0.0195	0.5768	22.2
0.0149	0.2443	12.3
0.00997	0.0000	0.0*
0.00677	0.0000	0.0
0.00369	0.0000	0.0
0.00281	0.0000	0.0

* Dilute solutions of thiourea in acid copper sulfate also precipitated the above complex, but the time required to do so was much longer, e.g. ~2 weeks for 10^{-3} M thiourea.

$$2\ CuSO_4 + 5\ Tu \rightarrow Cu_2SO_4.3Tu.H_2O + (H_4N_2CS\text{-})_2SO_4 \qquad (59)$$

This cuprous thiourea complex was insoluble in all common solvents, but seemed to dissolve to some extent, in concentrated nitric acid at 50-60°C.

When the complex was hydrolyzed by heating with 1 N NaOH, black crystals of cuprous sulfide (79.9% Cu) were formed (123). The yield of cuprous sulfide (33.5 to 34.3 wt % of the complex in four determinations) corresponded to that expected for the proposed monohydrate formula (33.89%).

The complex was soluble in aqueous thiourea solutions from which it could be recovered as pentathioureadicuprous sulfate dihydrate (c.f. Table 11 for analytical data).

The complex $Cu_2Tu_3SO_4H_2O$ became grey at about 180°C and melted with decomposition at 235°C. The infrared (Figure 22) and Raman (Figure 23) spectra indicated that the sulfate ions were not involved in any covalent or coordinate bonds. The ν_1 mode of $SO_4^=$ at 972 cm^{-1} appeared as a very weak band in the infrared whereas, it was one of the strongest bands observed in the Raman spectrum, as expected for a T_d symmetric stretching mode (124). Thus, if tetrahedral coordination is required for each cuprous ion, the basic formula unit would have to be $Cu_4Tu_6(SO_4)_2.2H_2O$, since this is the smallest grouping in which tetrahedral coordination can be achieved by the available thiourea. Such a structure would involve all

TABLE 11

ANALYSES OF CUPROUS-THIOUREA COMPLEX

Sample[a] (M)	% Cu	% S	% N	% C	% H
0.0763	26.12	26.32[b]	16.10[b]	7.51[b]	3.17[b]
0.0443	26.40	27.57	18.04	7.98	3.19
0.0254	26.24	26.89	17.58	7.72	3.13
0.0195	26.09	27.18	17.98	7.81	2.84
0.0149	26.43	26.61	18.20	8.11	3.10
0.00159[c]	26.35	27.05	18.07	8.01	3.23
0.000965	26.19	26.44	18.09	7.85	3.13
Average	26.31 ±0.25	26.87 ±0.44	18.02 ±0.17	7.64 ±0.20	3.12 ±0.20
Calculated[d]	27.07	27.76	17.89	7.67	2.98
Recrystallized from Thiourea	19.47		21.22	9.27	3.54
Calculated[e]	19.86		21.88	9.38	3.75

a) concentration of thiourea in standard electrolyte from which complex was isolated.

b) values by Schwarzkopf Microanalytical Laboratory

c) prepared in the presence of metallic copper

d) calculated for $Cu_2Tu_3SO_4.H_2O$

e) calculated for $Cu_2Tu_5SO_4.H_2O$

FIGURE 22

INFRARED ABSORPTION SPECTRUM OF
$Cu_2Tu_3SO_4.H_2O$ AS KBr DISK

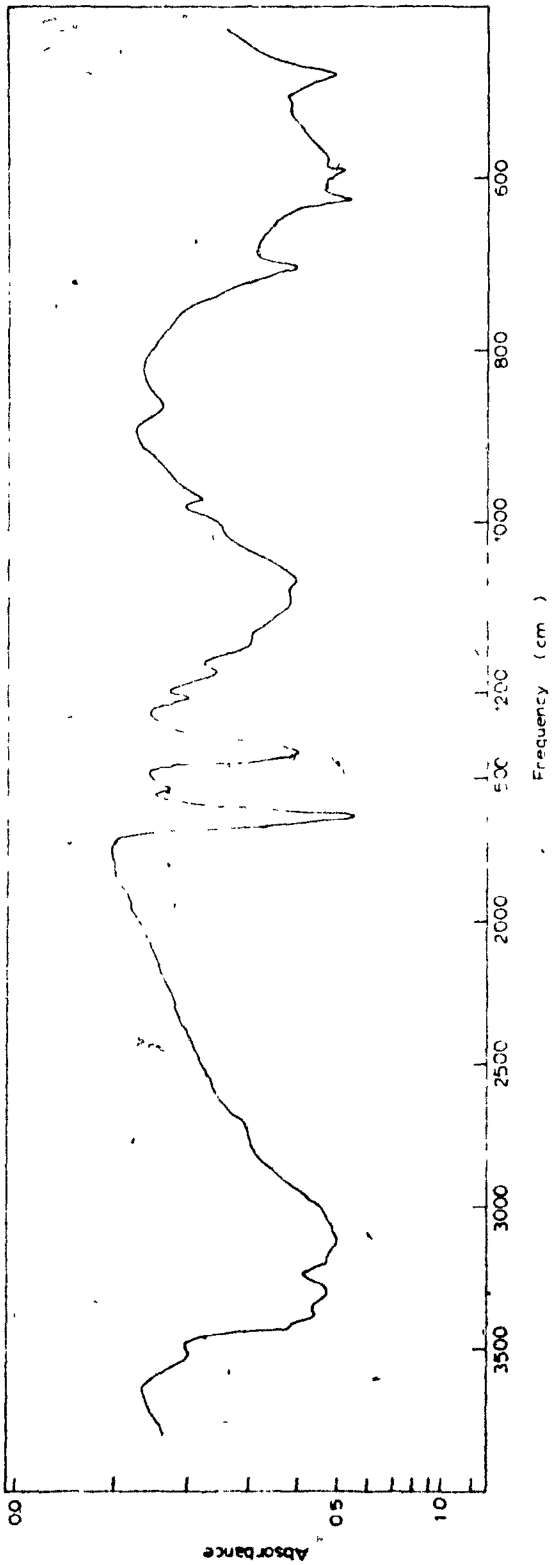

Absorbance
0.0
0.5
1.0
Frequency (cm)
600
800
1000
1200
1500
2000
2500
3000
3500

FIGURE 23

RAMAN SPECTRUM OF $Cu_2Tu_3SO_4H_2O$*

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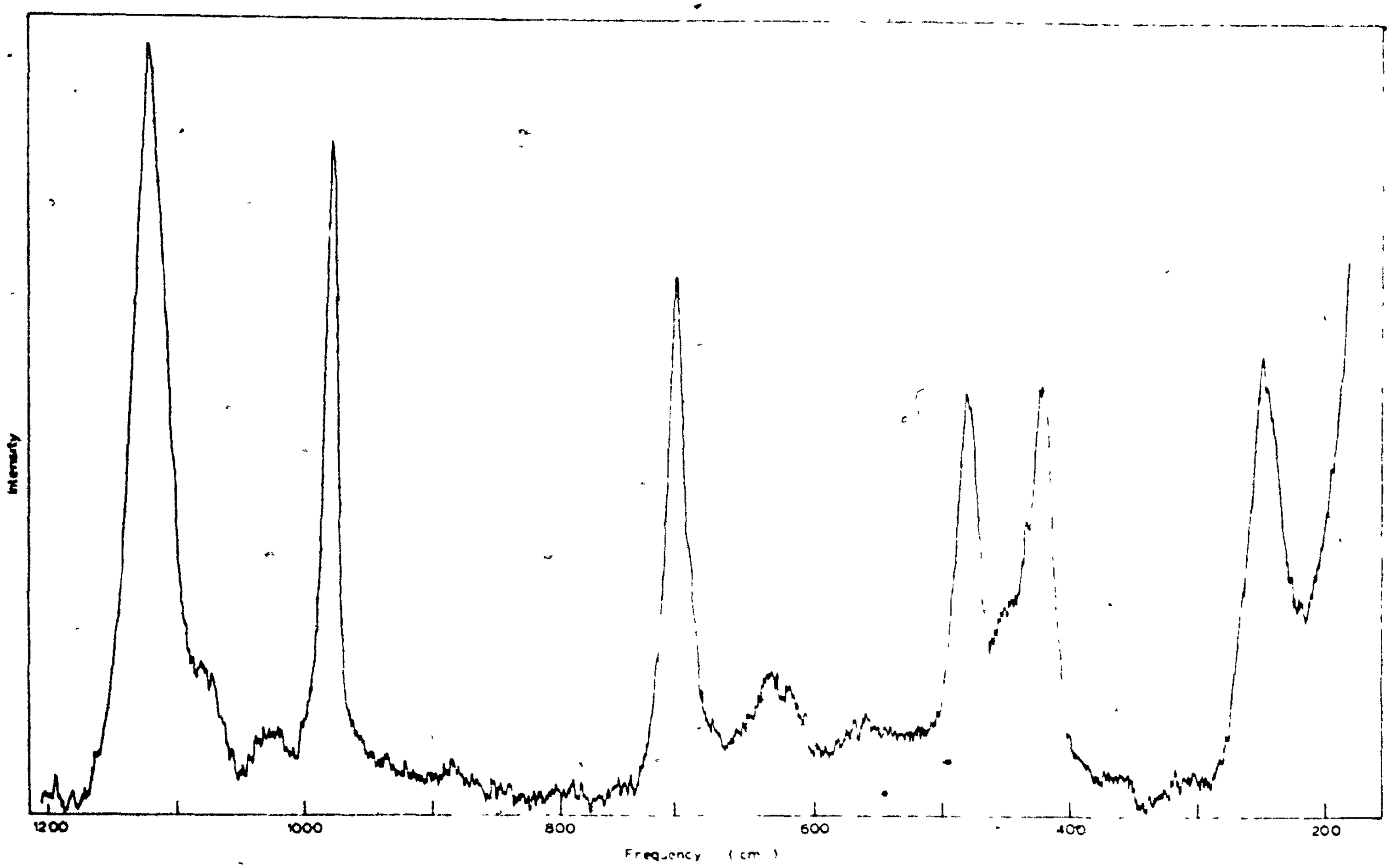
* Determined by Dr. G. Barna,
Department of Chemistry


Intensity
1200
1000
800
600
400
200
Frequency (cm⁻¹)

the thiourea sulfur atoms in electron-deficient three-center bridging bonds of the type Cu^{I}-S-Cu^{I}, but such bonds are a known possibility (115-117). The Raman spectrum also showed a sharp, strong band at 250 cm^{-1} which can be assigned to a Cu-S stretching mode (125,126).

IDENTIFICATION OF THE SPECIES RESPONSIBLE FOR THE ABSORPTION MAXIMUM AT 340 nm

In agreement with Hintermann and Javet (37) it was found that an absorption maximum at 340 nm appeared when thiourea was dissolved in acid cupric sulfate solutions initially free from cuprous ions. Since the band had been attributed to a cuprous-thiourea ion, it seemed reasonable that a solution of CuTuCl.½H_2O in dilute sulfuric acid should show the same absorption band. However, it was found that neither CuTuCl nor $CuTu_3Cl$ showed an absorption maximum in this region, although appreciable absorbance due to a peak at 236 nm was observed. This would seem to indicate that the absorbance maximum at 340 nm might not be due to a cuprous thiourea species.

The reaction between thiourea and cupric salts to give formamidinedisulfide and cuprous thiourea complexes is quite rapid, as evidenced by the apparently instantaneous reduction of $CuSO_4$(0.5 M $CuSO_4$,1 M H_2SO_4) by thiourea (0.5 M Tu, 1 M H_2SO_4). Nevertheless, it was considered possible that the absorption maximum at 340 nm might be due to a cupric-thiourea complex formed as an intermediate in the redox reaction. Since the reaction was very fast, the rate at which thiourea and copper sulfate solutions were mixed became a critical variable in any attempt to study the system.

When small volumes of concentrated thiourea solution were added to concentrated aqueous copper sulfate, there inevitably occurred a mixing zone that contained a higher concentration of thiourea than the final solution. This was probably responsible for the irreproducible absorbance-time behaviour observed under such conditions in the 300-400 nm range. However, the absorbance-time curve at 340 nm generally passed through a slight maximum, as reported by Hintermann and Javet.

When dilute thiourea solutions ($\lesssim 5 \times 10^{-3}$ M) were added to well agitated copper sulfate solutions, the absorbance-time behaviour at 340 nm no longer showed a maximum and became reproducible. This was interpreted as the rapid establishment of a quasi-equilibrium concentration of the species responsible for the absorption maximum at 340 nm, followed by a slow reaction that subsequently caused its depletion. Owing to the slow decrease of this quasi-equilibrium concentration with time, it was possible to determine the nature of the species involved, together with its extinction coefficient and stability constant.

The method developed by Job (104) was used to determine the copper-thiourea ratio in the complex. For the equilibrium*

$$mA + nB = A_m B_n \tag{60}$$

it has been shown (127) that a curve expressing the concentration of the complex, or a quantity proportional to the concentration, e.g. absorbance, as a function of the mole fraction of ligand $x = \frac{C_B}{C_A + C_B}$, (where c_i represents the concentration of species i) exhibited a maximum for $x = \frac{n}{m+n}$. It is possible, therefore, to determine the ligand-metal ratio for a complex which obeys Eqn. (60), with an equilibrium constant

$$K = \frac{[A_m B_n]}{[A]^m [B]^n} \tag{61}$$

If C represents the constant total concentration of reactants ($C = C_A + C_B$) and x the mole fraction of ligand, the equilibrium concentrations of A and B may be written

$$[A] = C(1-x) - m[A_m B_n] \tag{62}$$

$$[B] = Cx - n[A_m B_n] \tag{63}$$

Hence

---

* Job studied systems for which $m = 1$

$$\frac{1}{K}[A_mB_n] = (C(1-x) - m[A_mB_n])^m(x-n[A_mB_n])^n \qquad (64)$$

Substituting $[A_mB_n]/C = y$, Eqn. (64) may be written

$$f(x,y) = (1-x-my)^m(x-ny)^n - \frac{1}{KC^{m+n-1}}y = 0 \qquad (65)$$

Differentiating Eqn. (65) with $\frac{df(x,y)}{dx} = 0$, yields $x = \frac{n}{m+n}$ for the maximum in the curves of variation. For $m=n=1$ and $x=o$ or $x=1$, the derivative of Eqn. (65) becomes

$$\frac{dy}{dx} = \frac{1}{1+\frac{1}{KC}} \qquad (66)$$

However, for $m=n>1$, the derivative becomes $\frac{dy}{dx} = 0$ for $x=o$ or $x=1$. Thus, if a maximum at the mole fraction $x=0.5$ is obtained in a plot of absorbance against mole fraction, the presence or absence of inflections and the form and gradients of the curves for values of x near zero may give information about the group of 1:1 complex present (i.e. 1:1, 2:2 or possibly even 3:3). A curve which exhibits inflections and is parabolic for values of x near zero and one, and which has zero gradient at $x=o$, and $x=1$, indicates the presence of a complex with $m=n>1$. On the other hand, the absence of inflections and parabolic portions, together with a finite gradient at $x=o$ and $x=1$, indicate a complex with $m=n=1$.

The method of continuous variation was applied to mixtures of cupric sulfate and thiourea in 0.1 M H_2SO_4 for c=0.007, 0.010 and 0.020 M(Figure 24)Tables 12-14) and also in 0.1 M H_2SO_4, 0.9 M $(NH_4)_2SO_4$ for C=0.010 and 0.020 M (Tables 15, 16).

The maximum at x=0.5 and the finite slope at x=o and x=1 clearly indicate the formation of a complex between cupric sulfate and thiourea, with m=n=1. The effect of ammonium sulfate on the curves will be discussed later.

In application of the mole-ratio method, the total concentration of cupric sulfate was kept constant while the total concentration of the ligand was increased. Conversely, the total ligand concentration may be held constant while the total metal ion concentration is increased. In the former case, the absorbance due to the complex is plotted as a function of the total ligand concentration. If only one complex of high stability is formed, the graph consists of two linear intersecting parts. However, as the magnitude of the stability constant decreases, the break in the curve becomes more uncertain.

For cupric sulfate and thiourea in 0.1 M H_2SO_4 the curves show no sharp break, an indication that the complex has a low value for its association constant (Figure 25, Tables 17-19).

FIGURE 24

ABSORBANCE OF COMPLEX AT 340 nm FOR DIFFERENT MOLE FRACTIONS OF THIOUREA IN 0.1 M SULFURIC ACID SOLUTION

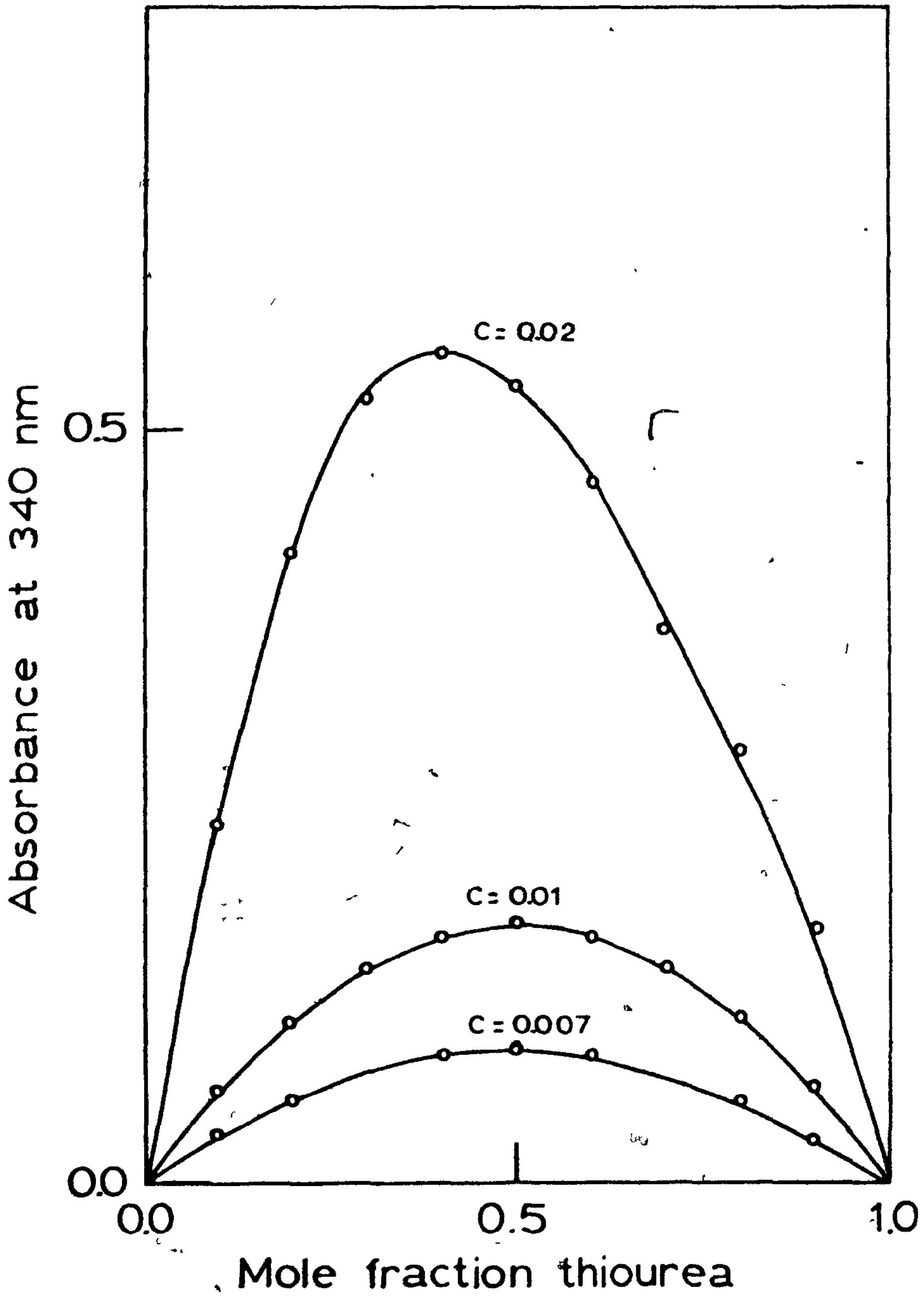

C= 0.02
C= 0.01
C= 0.007
0.5
0.0
Absorbance at 340 nm
0.0
0.5
1.0
Mole fraction thiourea

TABLE 12

ABSORBANCE OF COPPER COMPLEX AT 340 nm FOR DIFFERENT MOLE FRACTIONS, X, OF THIOUREA WITH C = 0.007 M IN 0.1 M H_2SO_4 AT 25°C

X	A_{340}	$K_{calc}(\varepsilon_{340}=3300)$
0.10	0.0339	2.41
0.20	0.0548	2.19
0.40	0.0852	2.27
0.50	0.0917	2.34
0.50	0.0893	2.29
0.60	0.0856	2.28
0.80	0.0572	2.29
0.90	0.0297	2.11

$K_{av} = 2.27 \pm 0.18$

TABLE 13

ABSORBANCE OF COPPER COMPLEX AT 340 nm FOR DIFFERENT MOLE FRACTIONS, X, OF THIOUREA WITH C = 0.010 M IN 0.1 M H_2SO_4 AT 25°C

X	A_{340}	$K_{calc}(\varepsilon_{340} = 3300)$
0.10	0.064	2.24
0.20	0.108	2.13
0.30	0.145	2.18
0.40	0.164	2.15
0.50	0.174	2.20
0.60	0.164	2.17
0.70	0.145	2.18
0.80	0.112	2.21
0.90	0.067	2.35

$K_{av} = 2.20 \pm 0.14$

TABLE 14

ABSORBANCE OF COPPER COMPLEX AT 340 nm FOR DIFFERENT MOLE FRACTIONS, X, OF THIOUREA WITH C = 0.020 M IN 0.1 M H_2SO_4 AT 25°C

X	A_{340}	$K_{calc}(\varepsilon_{340}=3300)$
0.10	0.240	2.10
0.20	0.420	2.07
0.30	0.521	1.95
0.40	0.551	1.80
0.50	0.532	1.66
0.60	0.468	1.52
0.70	0.372	1.37
0.80	0.290	1.41
0.90	0.172	1.49

$K_{av} = 1.71 \pm 0.32$

TABLE 15

ABSORBANCE OF COPPER COMPLEX AT 340 nm FOR DIFFERENT MOLE FRACTIONS, X, OF THIOUREA WITH $C = 0.010\ \underline{M}$ IN $0.1\ \underline{M}\ H_2SO_4$ $0.9\ \underline{M}\ (NH_4)_2SO_4$ AT 25°C

X	A_{340}	$K_{calc}(\varepsilon_{340}=3300)$
0.05	0.020	1.30
0.10	0.053	1.82
0.20	0.083	1.60
0.30	0.109	1.60
0.40	0.120	1.54
0.50	0.125	1.54
0.60	0.121	1.55
0.70	0.110	1.61
0.80	0.087	1.68
0.90	0.053	1.82

$K_{av} = 1.55 \pm 0.26$

TABLE 16

ABSORBANCE OF COPPER COMPLEX AT 340 nm FOR DIFFERENT MOLE FRACTIONS, X, OF THIOUREA WITH C = 0.020 M IN 0.1 M H_2SO_4 0.9 M $(NH_4)_2SO_4$ AT 25°C

X	A_{340}	$K_{calc}(\varepsilon_{340}=3300)$
0.10	0.290	2.57
0.20	0.421	2.08
0.30	0.504	1.89
0.50	0.522	1.63
0.60	0.510	1.67
0.70	0.347	1.70
0.80	0.376	1.85
0.90	0.260	2.29

$K_{av} = 1.96 \pm 0.58$

The dilution method developed by Sanioto and Cilenti (128) was applied to the system to determine K_{eq} and ε_{340}.

For a weak complex formed by the reaction

$$A + B = C \tag{67}$$

the equilibrium constant is

$$K = \frac{[C]}{[A][B]} \tag{68}$$

If m_i denotes the number of moles of species i present in the solution of volume V, i.e. $[X_i] = \frac{m_i}{V}$, the equilibrium concentrations of the individual species for the condition $m_B >> m_A > m_C$, may be written

$$[A] = \frac{m_A - m_C}{V} \tag{69}$$

$$[B] = \frac{m_B - m_C}{V} \simeq \frac{m_B}{V} \tag{70}$$

$$[C] = \frac{m_C}{V} = \frac{A_\lambda}{\varepsilon_\lambda} \tag{71}$$

In Eqn. (71), A_λ is the corrected absorbance due to the complex at the wavelength λ, and ε_λ is the molar absorptivity of the complex at that wavelength. Substituting these values into Eqn. (68), and rearranging,

FIGURE 25

MOLE RATIO METHOD APPLIED TO COPPER SULFATE AND THIOUREA IN SOLUTION OF 0.1 M SULFURIC ACID

Legend

o - [Tu] = constant = 0.005 M, B = [$CuSO_4$]

Δ -[$CuSO_4$]= constant = 0.005 M, B = [Tu]

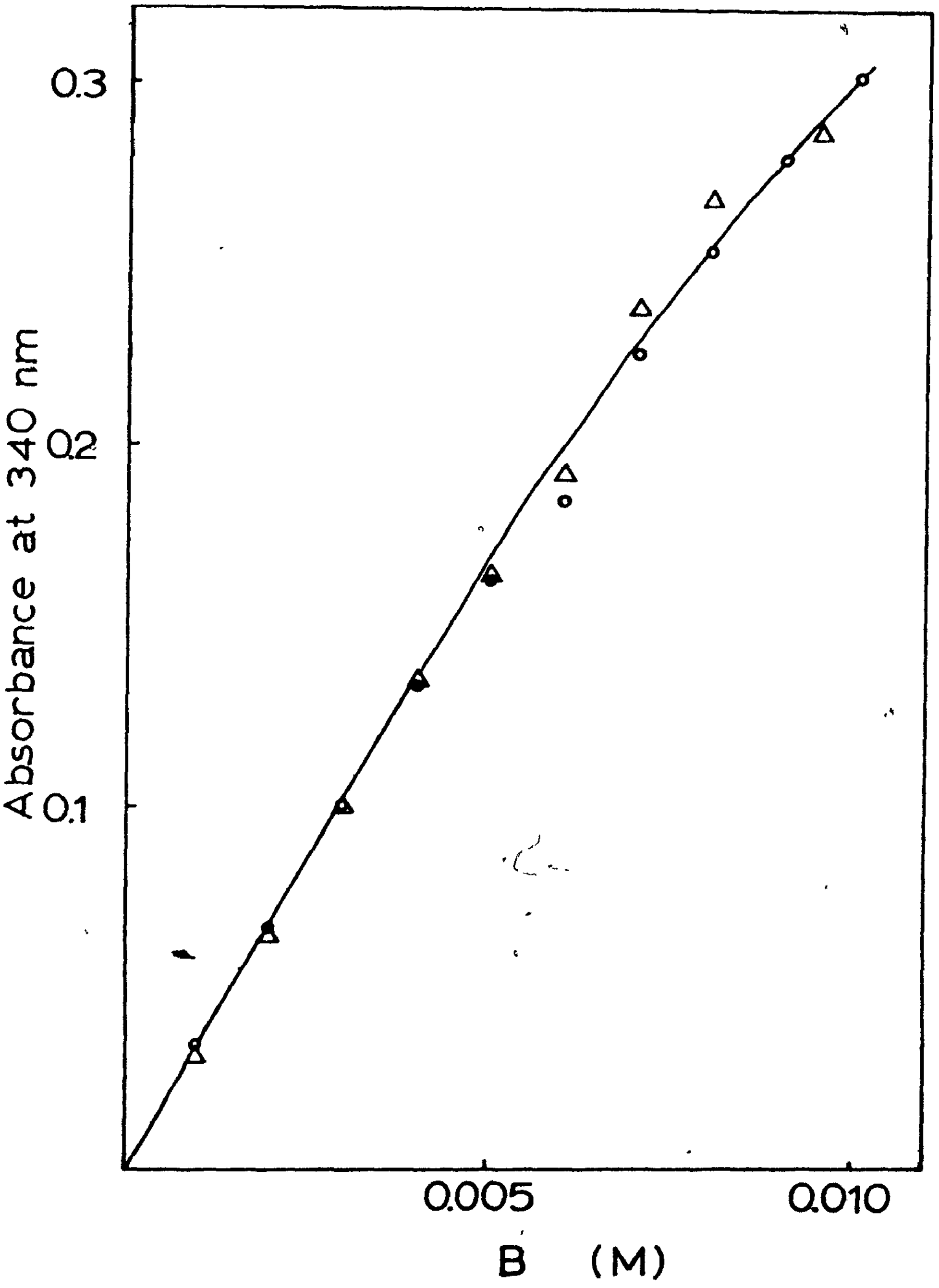

Absorbance at 340 nm
0.3
0.2
0.1
0.005
0.010
B (M)

TABLE 17

ABSORBANCE OF COPPER COMPLEX AT 340 nm FOR DIFFERENT TOTAL CONCENTRATIONS OF COPPER SULFATE WITH A TOTAL THIOUREA CONCENTRATION OF 0.005 M IN 0.1 M H_2SO_4 AT 25°C

$[CuSO_4]$	A_{340}	K_{calc}
0.0010	0.034	2.13
0.0020	0.067	2.10
0.0030	0.101	2.11
0.0040	0.134	2.11
0.0050	0.163	2.05
0.0060	0.185	1.94
0.0070	0.225	2.03
0.0080	0.254	2.01
0.0090	0.280	1.97
0.0100	0.301	1.91

$K_{av} = 2.04 \pm 0.10$

TABLE 18

ABSORBANCE OF COPPER COMPLEX AT 340 nm FOR DIFFERENT TOTAL CONCENTRATIONS OF THIOUREA WITH A TOTAL COPPER SULFATE CONCENTRATION OF 0.005 M IN 0.1 M H_2SO_4 AT 25°C

[Tu]	A_{340}	$K_{calc}(\varepsilon_{340}=3300)$
0.0010	0.030	1.87
0.0020	0.065	2.04
0.0030	0.101	2.11
0.0040	0.137	2.16
0.0050	0.166	2.09
0.0060	0.197	2.07
0.0070	0.238	2.15
0.0080	0.268	2.13
0.0095	0.286	1.91

$K_{av} = 2.06 \pm 0.10$

TABLE 19

ABSORBANCE OF COPPER COMPLEX AT 340 nm FOR DIFFERENT COPPER SULFATE CONCENTRATIONS WITH A TOTAL THIOUREA CONCENTRATION OF 0.00205 M IN 0.1 M H_2SO_4 AT 25°C

$[CuSO_4]$	A_{340}	$K_{calc}(\varepsilon_{340}=3300)$
0.005	0.075	2.30
0.010	0.146	2.26
0.020	0.272	2.14
0.050	0.600	1.99
0.125	1.290	1.93

$K_{av} = 2.12 \pm 0.18$

$$\frac{K\ m_A\ m_B}{V^2} - \frac{K\ m_B\ \frac{\Delta_\lambda V}{\varepsilon\lambda}}{V^2} = \frac{A_\lambda}{\varepsilon_\lambda} \tag{72}$$

Multiplication of this last equation by $\frac{\varepsilon_\lambda}{A_\lambda}$ V gives

$$V = -\ K\ m_B + \frac{K\varepsilon_\lambda\ m_A\ m_B}{VA_\lambda} \tag{73}$$

If m_A and m_B are kept constant and the absorbance, A_λ, of the complex determined as a function of the volume of the solution, the association constant and molar absorptivity may be determined from a plot of V against $\frac{1}{VA_\lambda}$.

The data for optimum concentrations of copper sulfate and thiourea are shown in Table 20, and plotted in Figure 26.

From the least-mean-squares line, values of K = 2.37 and ε_{340} = 3320 were obtained, with an estimated error of ± 5%. The same method applied to copper sulfate and thiourea in 0.1 M H_2SO_4, with $(NH_4)_2SO_4$ (0.9 M) present, gave K = 1.43 and ε_{340} = 3340 (Table 21).

The lower apparent association constant in the presence of ammonium sulfate may be explained by a shift in the equilibrium

$$Cu^{2+}_{aq} + SO_4{}^{=}{}_{aq} = CuSO_4{}_{aq} \tag{74}$$

FIGURE 26

DILUTION METHOD APPLIED TO CUPRIC SULFATE
(5×10^{-3} MOLES) AND THIOUREA (6×10^{-6} MOLES)
IN 1.0 M SULFURIC ACID SOLUTION

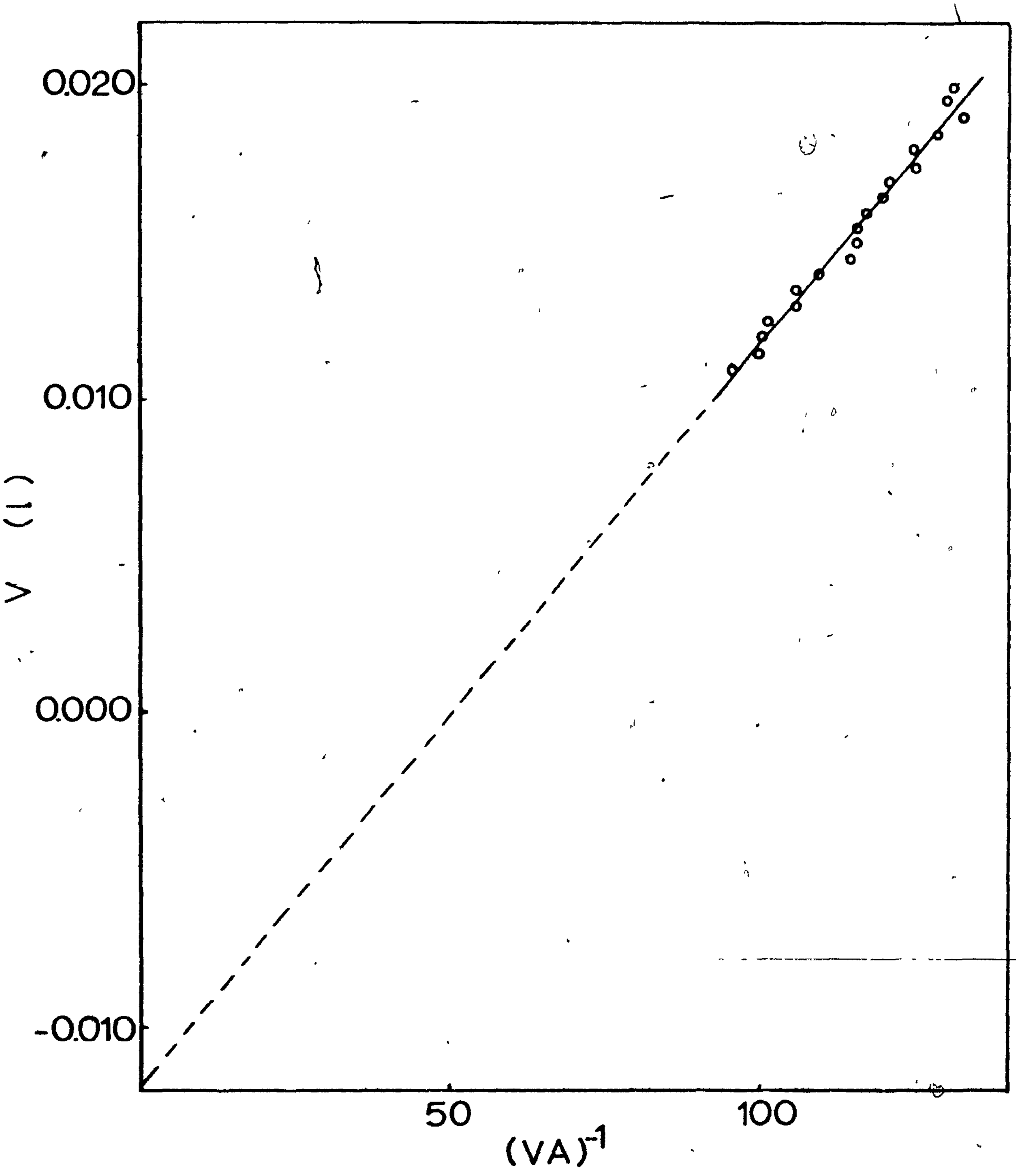

0.020
0.010
0.000
-0.010
V (1)
50
100
(VA)$^{-1}$

TABLE 20

ABSORBANCE OF COPPER COMPLEX AT 340 nm FOR DIFFERENT TOTAL VOLUMES OF SOLUTION CONTAINING 5×10^{-3} MOLES TOTAL COPPER SULFATE AND 6×10^{-6} MOLES TOTAL THIOUREA IN 1.0 M H_2SO_4 AT 25°C

V (ℓ)	A_{340}	$\frac{1}{VA_{340}}$
0.0110	0.950	95.7
0.0115	0.870	100.0
0.0120	0.830	100.5
0.0125	0.790	101.3
0.0130	0.730	105.4
0.0135	0.700	105.8
0.0140	0.650	109.9
0.0145	0.600	115.0
0.0150	0.575	116.0
0.0155	0.556	116.0
0.0160	0.531	117.6
0.0165	0.505	120.0
0.0170	0.486	121.0
0.0175	0.457	125.0
0.0180	0.444	125.1
0.0185	0.419	129.0
0.0190	0.395	133.1
0.0195	0.393	130.5
0.0200	0.380	131.6

LMS line $V = -\ 0.01185 + 0.0002364\ \frac{1}{VA_{340}}$

TABLE 21

ABSORBANCE OF COPPER COMPLEX AT 340 nm FOR DIFFERENT TOTAL VOLUMES OF SOLUTION CONTAINING 1×10^{-3} MOLES TOTAL COPPER SULFATE AND 1×10^{-5} MOLES TOTAL THIOUREA IN 0.1 M H_2SO_4, 0.9 M $(NH_4)_2SO_4$ AT 25°C

V (ℓ)	A_{340}	$\frac{1}{VA_{340}}$	$K_{calc.}$
0.0110	0.349	260	1.45
0.0130	0.248	310	1.41
0.0141	0.220	322	1.47
0.0150	0.191	349	1.43
0.0170	0.149	395	1.42
0.0210	0.098	488	1.40

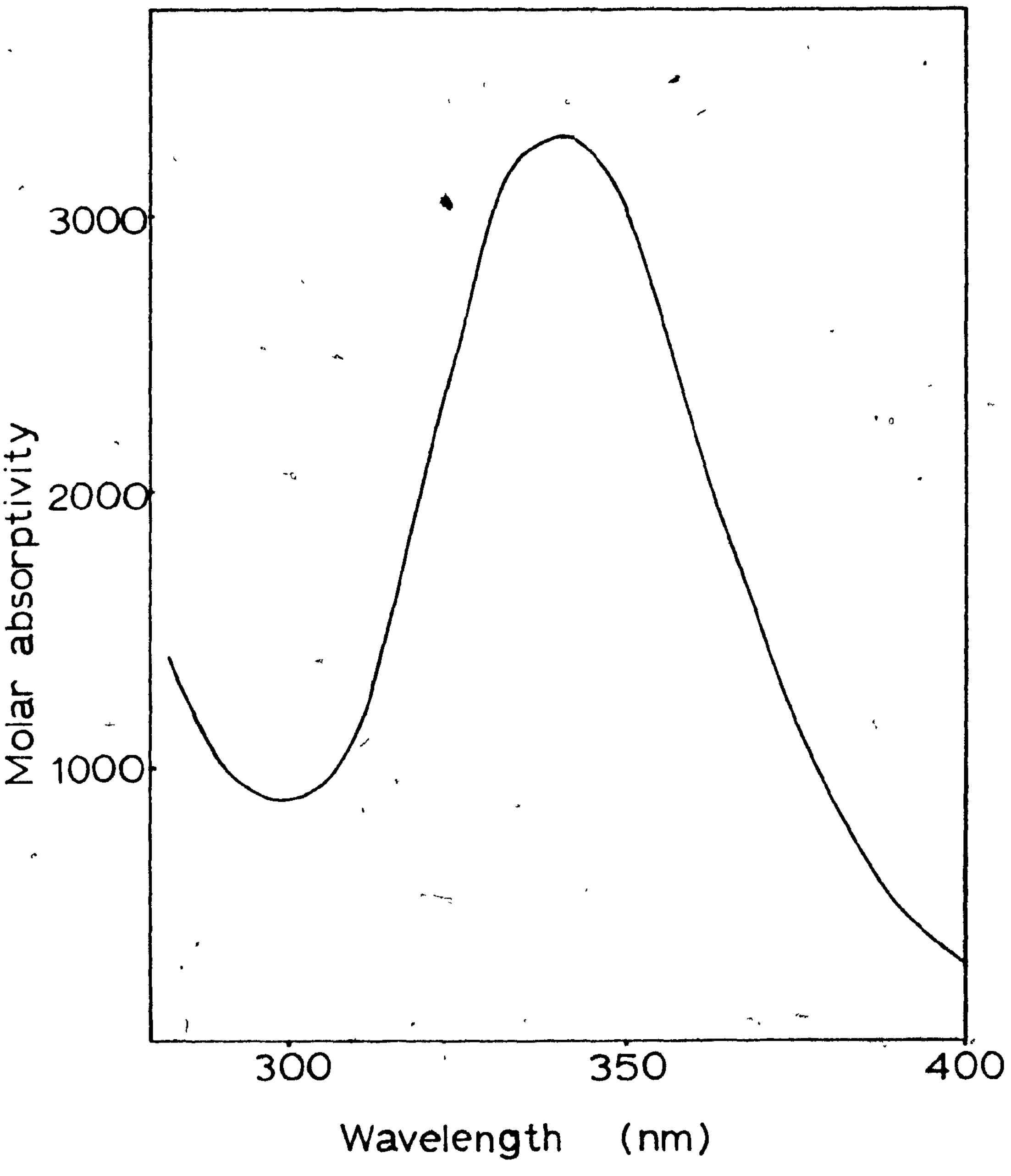
Since HSO_4^- is a weak acid, the solution containing $(NH_4)_2SO_4$ has a higher concentration of $SO_4^=$ than sulfuric acid solution of equal total sulfate concentration. Consequently, there should be fewer free cupric ions in the presence of added $(NH_4)_2SO_4$ than in its absence for given sulfuric acid concentration. The concentration of a weak complex of thiourea with free cupric ion should therefore be decreased in the presence of ammonium sulfate. The observed decrease in concentration of the complex that absorbs at 340 nm with addition of $(NH_4)_2SO_4$ is therefore in accord with a cupric-ion-thiourea complex, rather than a neutral cupric sulfate-thiourea species.

Values of the equilibrium constant, K, were also calculated by evaluating the concentrations of the complex from its molar absorptivity, $\varepsilon_{340} = 3300\ M^{-1}cm^{-1}$. The values obtained were $K = 2.2 \pm 0.2$ for sulfuric acid media and $K = 1.6 \pm 0.2$ when ammonium sulfate was present. The consistent values of K obtained over a wide range of concentrations lend support to the view that the band (Fig. 7) is due to a cupric thiourea complex, rather than some other species.

An attempt was made to determine the equilibrium constant for the formation of the Cu^{2+} - thiourea complex from the low intensity absorption ($\varepsilon_{800} \simeq 12$) due to copper sulfate in the long wavelength region. Unfortunately, it

FIGURE 27

UV ABSORPTION SPECTRUM OF THE CUPRIC ION-
THIOUREA COMPLEX WITH MAXIMUM ABSORBANCE
AT 340 nm


3000
2000
1000
Molar absorptivity
300
350
400
Wavelength (nm)

was not measurably affected by the presence of small concentrations of thiourea, and no estimate of the equilibrium constant was possible. However, the behaviour supports the view that the complex has a low stability constant.

An attempt was also made to determine the change in the activity of the Cu^{2+} ion with a cupric ion electrode (Orion, Model 94-29) when thiourea was added to a solution of cupric sulfate (10^{-3} to 10^{-6} M) in 0.1 M H_2SO_4. However, the potentials appeared to bear no relation to cupric ion activity, and this was also true when the potentials at a copper foil electrode were measured.

From the time dependence of the absorbance in the range 280 to 370 nm and a knowledge of the molar absorptivities of Cu^{2+} SCN_2H_4, SCN_2H_4 and formamidinedisulfide , it was concluded that, at time $t > 0$, the absorbance in the region below 340 nm was too large and increased too rapidly to be accounted for by the above species only. However, since it had been shown earlier that the compounds CuTuCl and $CuTu_3Cl$ in sulfuric acid solution possess considerable absorbance in this region, it was considered that the absorbance which could not be accounted for could be due to a cuprous-thiourea complex. Thus, at time $t > 0$, the observed absorbance at 340 nm was a superposition of absorbances due mainly to the complexes $[Cu^{+}Tu]$ and $[Cu^{2+}Tu]$. This makes an exact interpretation of the absorbance at times other than $t \approx 0$

impossible, since the molar absorptivity of the complex $Cu^{+}SCN_{2}H_{4}$ in this medium was not known and could not be estimated unambiguously. This superposition of absorbances would seem to explain the complex absorbance-time behaviour found by Hintermann and Javet and in the present work under conditions where significant reaction occurs during mixing to give cuprous-thiourea complexes.

PREPARATION OF DICHLOROBIS (TETRAMETHYLTHIOUREA) COPPER II

When an aqueous solution of 1,1,3,3-tetramethyl-2-thiourea (TMT) was added to an aqueous solution of a cupric salt (sulfate, chloride, perchlorate, nitrate or acetate) a deep red color developed immediately and faded within a few seconds when the solution was shaken. From the UV spectrum of an appropriately diluted solution of TMT in acid cupric chloride, it was apparent that the TMT was rapidly and completely oxidized to di-(tetramethylformamidine)disulfide. It would seem that the red color that appeared when the solutions were mixed may be attributed to an absorbance band of a cupric ion- TMT complex, and that the color faded when rapid reaction occurred to give the disulfide together with cuprous ions that were oxidized by atmospheric oxygen.

Analogy with the corresponding cupric-thiourea reaction suggests that, if the reactants are mixed in initially neutral aqueous solution, the disulfide formed by oxidation presumably undergoes rapid hydrolysis to regenerate TMT. In the cycle of oxidation and hydrolysis reactions that ensues, the hydrolysis is inhibited by the accompanying decrease in pH. It is possible to break this cycle in concentrated solution by precipitation of the solid complex $CuCl_2.2TMT$ and it was, in fact, prepared by this method (118) before the oxidation-hydrolysis cycle was recognized.

When solutions of TMT and cupric chloride in isopropanol were mixed, the red color of the complex did not fade and a crystalline precipitate of deep red needles (mp 114-116°C) was obtained (c.f. Table 22 for analyses). The solution retained its red color for more than five days, indicating a drastic decrease in the rate of the rapid redox reaction relative to that which occurs in aqueous solution.

The absorbance of the solution of TMT and cupric chloride in isopropanol showed a complex behaviour. There appeared to be two overlapping absorption bands at 410 and 520 nm, with residual absorbance extending to approximately 700 nm. The observed red color of the solution was undoubtedly due to the broad complex band, combined with a decrease in the intensity of the long wavelength absorbance of $CuCl_2$.

It may be suggested tentatively that the effect of TMT concentration on the absorbances at 410 and 520 nm, at constant $CuCl_2$ concentration, might reflect the presence of a species such as $CuCl_2.TMT$ that is mainly responsible for

TABLE 22

A. REACTION OF CUPRIC CHLORIDE WITH TETRAMETHYL-THIOUREA IN ISOPROPANOL AT 25°C.

$CuCl_2$ millimole	tetramethyl thiourea millimole	$CuCl_2.2TMT$ millimole	$CuCl_2.2TMT$ (g)
1.00	1.00		0.2233
1.00	2.00	0.83	0.3299
1.00	3.00	0.84	0.3329
1.00	4.00	0.80	0.3171

B. ANALYSIS OF $CuCl_2.2TMT$

Element-%	Found	Calculated*
Cu	16.00	15.93
C	29.86	30.08
H	6.10	6.02
Cl	18.03	17.77

* Calculated values are for $CuCl_2.2TMT$
mol.wt. 398.90

the band at 410 nm, and a second species such as $CuCl_2.2TMT$ that is responsible for the absorbance at 520 nm with higher TMT concentrations. (Figures 28,29,Table 23). The complications appeared to be too formidable to attempt a quantitative interpretation of the system. It might well be that reactions in solvents of low ionizing power might permit isolation of tetra-N-alkylthiourea complexes with cupric salts, but the subject was not pursued further, since it did not seem relevant to any practicable aspects of copper electrodeposition.

DISCUSSION

On the basis of the experimental evidence obtained, it would seem that the band observed by Javet and Hintermann in solutions of thiourea and cupric sulfate, and attributed by them to a cuprous-thiourea complex, is in reality due to a cupric-thiourea complex.

McAuley and Gomwalk (78,79) have claimed that formation of significant concentrations of metal-thiourea complexes as intermediates in the metal ion oxidation of thioureas is unlikely under acid conditions such as used in the present study. This argument is based on a pK_a of + 2.03 (129) for the conjugate acid of thiourea, which is to be compared with a value of - 1.2 (93,94), confirmed in the present study.

TABLE 23

EFFECT OF TETRAMETHYLTHIOUREA CONCENTRATION ON THE SPECTRUM OF ITS SOLUTIONS WITH 2 x 10^{-4} M $CuCl_2$ IN ISOPROPANOL

[TMT] M	(A_{410})obs.	(A_{520})obs.
0.00000	0.042	0.000
0.00010	0.056	0.010
0.00020	0.072	0.014
0.00030	0.074	0.016
0.00040	0.074	0.018
0.00100	0.076	0.026
0.0020	0.080	0.032
0.0030	0.074	0.034

FIGURE 28

ABSORPTION SPECTRA OF ISOPROPANOL SOLUTIONS CONTAINING CUPRIC CHLORIDE (2 x 10^{-4} M) AND TMT

1) [TMT] = 0.0002 M

2) [TMT] = 0.003 M

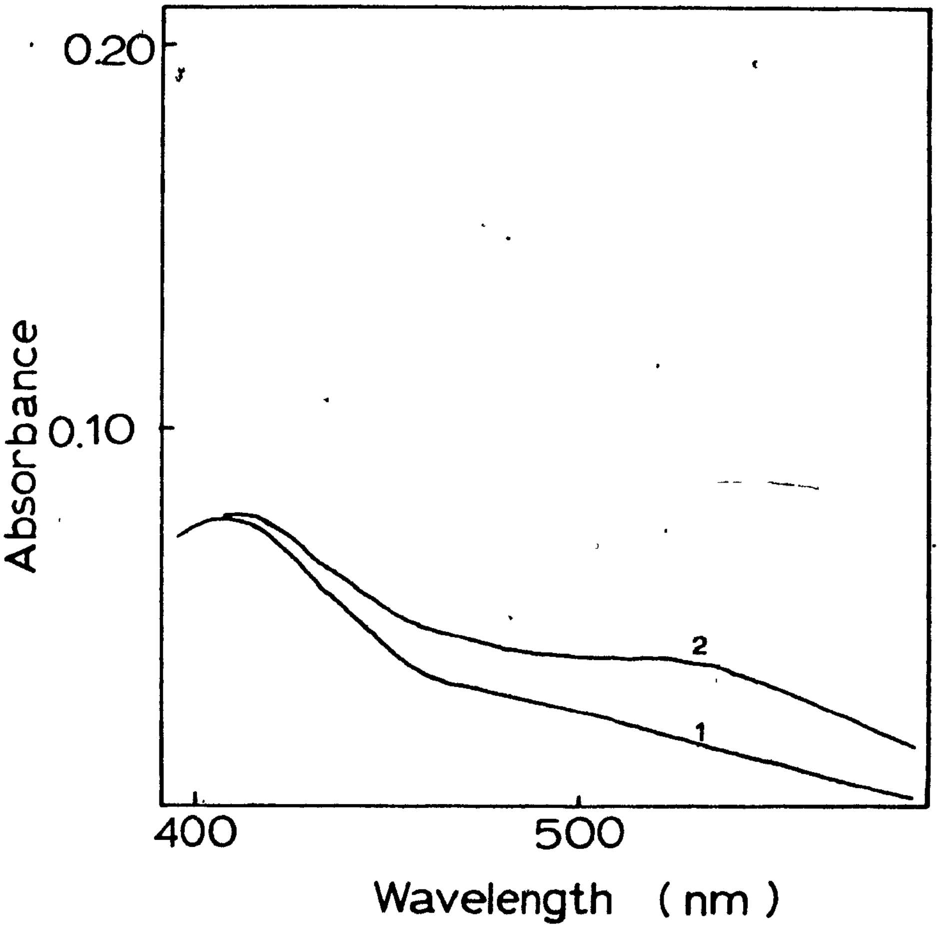
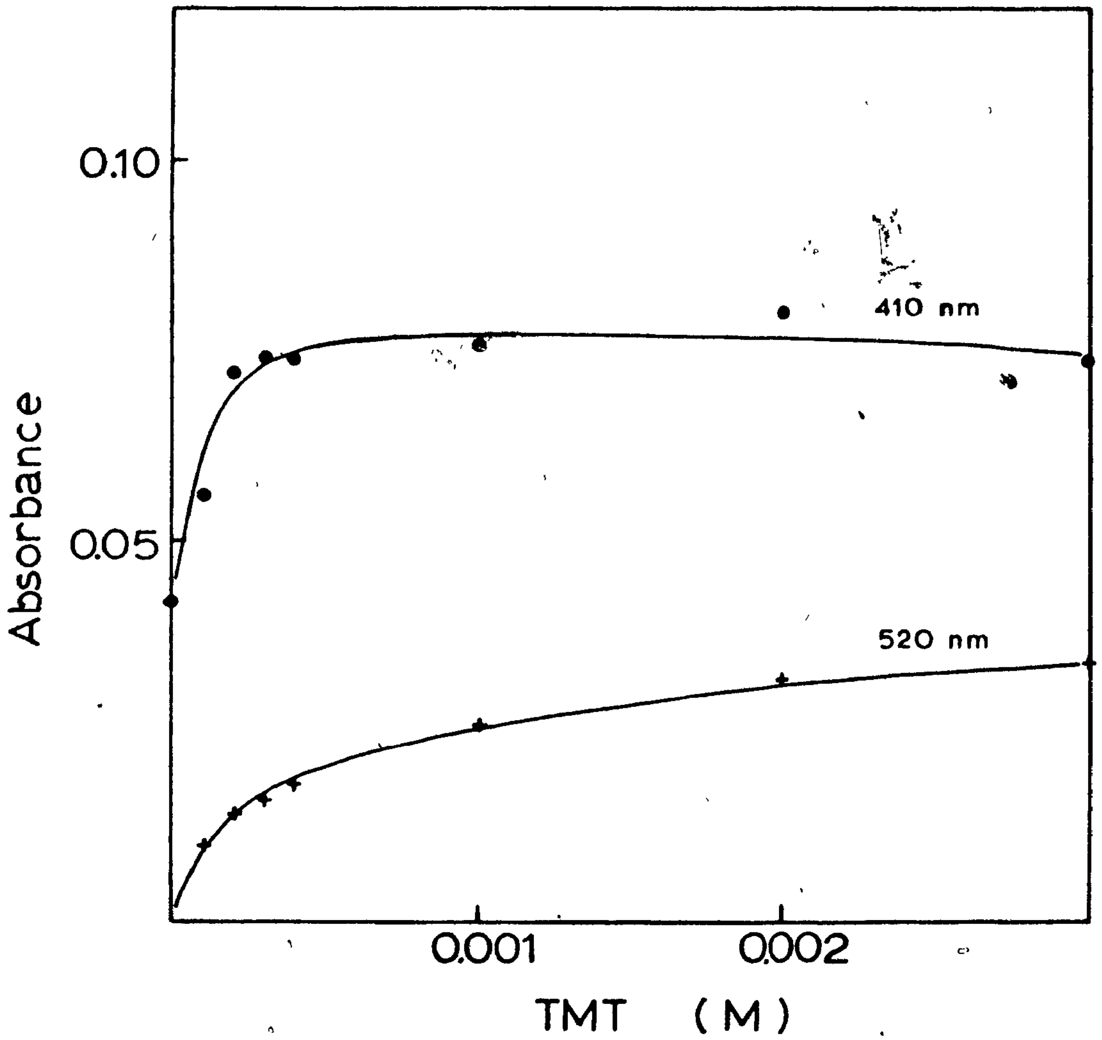

0.20
0.10
Absorbance
400
500
Wavelength (nm)
1
2

FIGURE 29

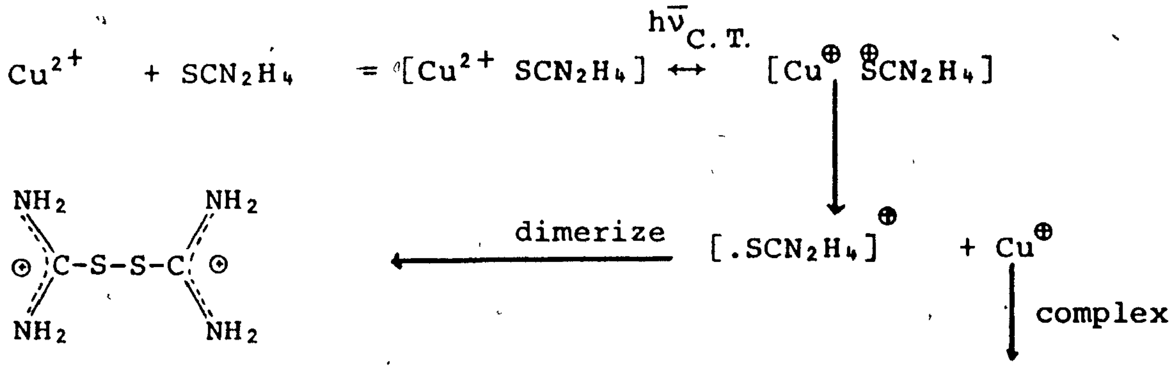
VARIATION WITH TMT CONCENTRATION OF THE ABSORBANCES AT 410 AND 520 nm OF ISOPROPANOL SOLUTIONS CONTAINING CUPRIC CHLORIDE (0.0002 M)


0.10
0.05
Absorbance
410 nm
520 nm
0.001
0.002
TMT (M)

In aqueous solution of cobalt II to which thiourea has been added, a band at 323 nm has been attributed to a charge transfer band of a cobalt II - thiourea complex (130). It has also been shown that N-alkylthioureas and iodine in dichloromethane solution show charge transfer bands in the region 310 nm (131). By analogy, it may be assumed that the band observed at 340 nm in thiourea-copper sulfate solutions is a charge transfer band corresponding to the transfer of an electron from the thiourea sulfur atom (donor) to the cupric ion (acceptor). The most elementary theory of charge transfer complexes predicts that, for such complexes with a given acceptor, the frequency of the charge transfer band should depend linearly on the ionization potential of the ligand (132). Thus, assuming hydration, stereochemistry, bond strength and similar factors to remain relatively constant, N-alkylthioureas in copper sulfate solution should give rise to charge transfer frequencies linearly related to the ionization potentials of the thioureas.

Hintermann and Javet (133) have determined λ_{max} values for solutions of various methylsubstituted thioureas in acid copper sulfate, and the corresponding ionization potentials have been determined independently (134). The values (Table 24, Figure 30) show a reasonably linear correlation, an indication that the assignment of these bands as charge-transfer bands in sulfur-coordinated cupric ion-thiourea complexes is correct.

In aqueous solution these cupric-thiourea complexes are intermediates in the reaction to give cuprous-thiourea complexes and formamidinedisulfides according to the sequence



With cupric chloride and tetramethylthiourea in isopropanol, the complex presumably must form with unionized cupric chloride. The low ionizing power of the solvent appears too weak to overcome coulombic attraction forces in the dissociative inner complex $CuCl_2^{\ominus}.^{\oplus}SCN_2Me_4$, which, therefore, reverts to the associative outer complex $Cu\ Cl_2.SCN_2Me_4$. On the other hand, the redox reaction can proceed in aqueous solutions as it does for thiourea, itself. Dimerization of the isothiouronium ion radicals to give formamidiniumdisulfides occurs in spite of the colombic repulsion forces, possibly because of the relatively large size of the ions involved (135).

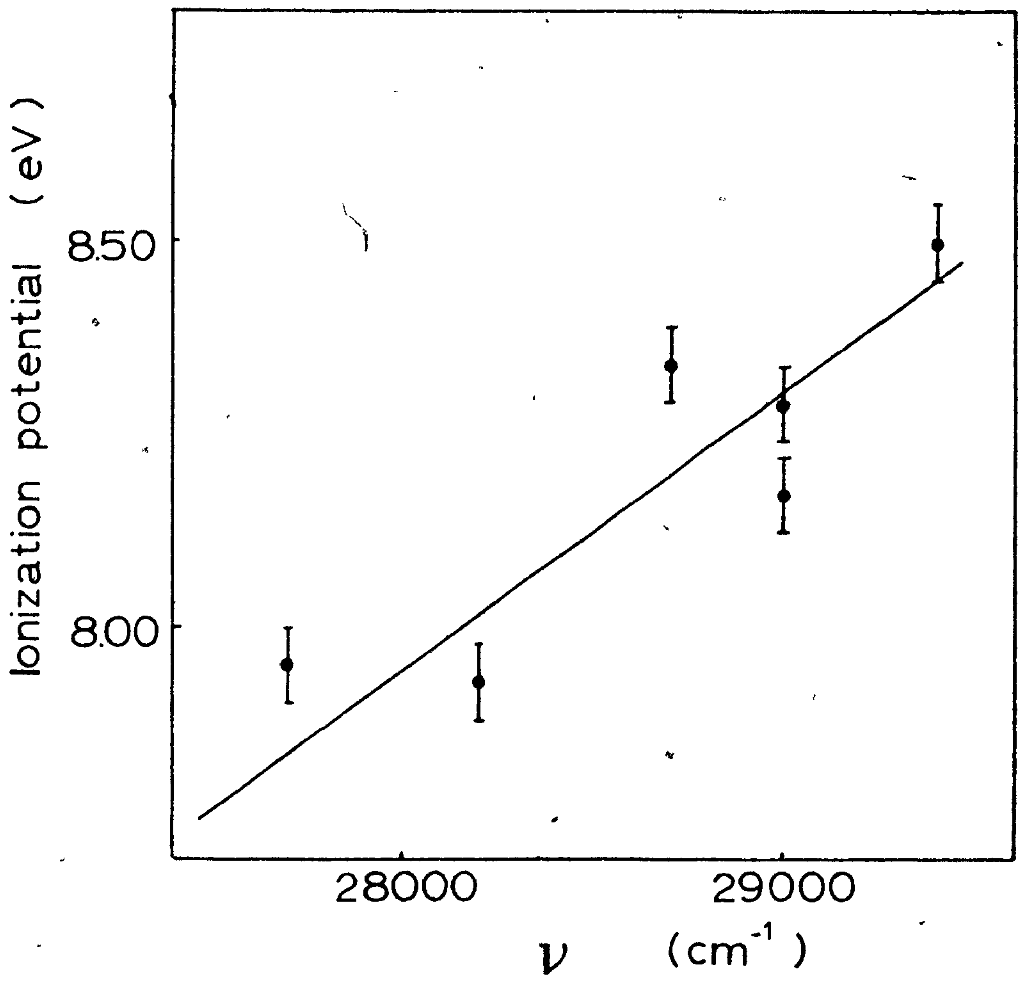
TABLE 24

RELATION BETWEEN λ_{max} (ν_{max}) FOR CUPRIC ION-THIOUREA COMPLEX ION AND IONIZATION POTENTIALS FOR THE CORRESPONDING THIOUREAS

Ligand	Ligand I.P. eV	ν_{max} C.T. kK
$NH_2.CS.NH_2$	8.50 ± 0.05	29.4
$NH_2.CS.NHCH_3$	8.29 ± 0.05	29.0
$NH_2.CS.N(CH_3)_2$	8.34 ± 0.05	28.7
$CH_3NH.CS.NHCH_3$	8.17 ± 0.05	29.0
$CH_3NH.CS.N(CH_3)_2$	7.93 ± 0.05	28.2
$(CH_3)_2N.CS.N(CH_3)_2$	7.95 ± 0.05	27.7

FIGURE 30

RELATION BETWEEN THE IONIZATION POTENTIALS OF VARIOUS SUBSTITUTED THIOUREAS AND THE FREQUENCIES OF THE CHARGE TRANSFER BANDS OF THE CORRESPONDING THIOUREA COMPLEXES WITH CUPRIC ION IN AQUEOUS SULFURIC ACID



Ionization potential (eV)
8.50
8.00
28000
29000
ν (cm^{-1})

ELECTROCHEMICAL BEHAVIOUR OF FORMAMIDINE-DISULFIDE AND COMPLEXES OF THIOUREA DURING ELECTRODEPOSITION OF COPPER

INTRODUCTION

Changes in the overpotential caused by thiourea during deposition of copper from acid copper sulfate solutions have been studied for both unstirred (convective mixing) and stirred (rotating disk electrode) conditions.

Early investigations in unstirred solutions demonstrated large overpotential increases. Shreier and Smith (28) found that the presence of 10^{-4} M thiourea, at a current density of 2.0 A/dm^2, increased the overpotential by approximately 140 mV. Similar values were obtained by other workers (41), but the polarization was very irreproducible and varied with age of the solution.

In sharp contrast, at 1 A/dm^2 in unstirred acid copper sulfate solution, Raub and Schiffner (38) found that 5×10^{-3} M thiourea caused an overpotential increase of only 25 mV after 20 minutes of electrolysis and approximately 30 mV after 40 minutes. Because of fluctuations in overpotential with more than 3×10^{-3} M thiourea they were unable to obtain Tafel plots for these systems. Also in unstirred electrolyte, at 50°C, Lahousse and Heerman (35) found 2.5×10^{-4} M thiourea to increase the polarization at 3 A/dm^2 by approximately 400 mV, but to cause almost no change at 2 A/dm^2. The data did not give a linear Tafel plot.

Turner and Johnson (32) studied the effects of thiourea on cathode polarization in unstirred acid copper sulfate solution, and also at a rotating disk electrode. In unstirred solution, at 2.0 A/dm^2, the presence of 4 x 10^{-4} M thiourea was found to increase the polarization by only 20 mV while lower concentrations of 4 x 10^{-5} and 4 x 10^{-6} M caused depolarization of approximately 20 and 45 mV respectively. In the same electrolyte at the same current density, but with a disk electrode rotating at 100 or 400 r.p.m., their data showed only a slight depolarizing effect for 1.3 x 10^{-4} M thiourea (33). No allowance was made in either study for attainment of steady state conditions. Changes in Tafel plots were interpreted to indicate that thiourea delayed a transition of the rate-determining step, as the current density was increased, from one of surface diffusion of adatoms to one of charge transfer (32). It was proposed that the thiourea molecule was reduced to ammonium cyanide and hydrogen sulfide. The hydrogen sulfide then formed cupric sulfide that precipitated onto the electrode because of the low solubility product of copper sulfide. Apparently, however, hydrogen cyanide has never been detected in these systems, which casts doubt on the proposed scheme.

Polarization measurements using a disk electrode rotating at speeds of 360 or 900 r.p.m., in acid copper sulfate solutions containing 2.5 x 10^{-4} and 3.9 x 10^{-4} M thiourea, gave overpotential increases of the order of 100 to

140 mV over the range 0.5 to 3 A/dm^2 (136). These values are comparable with the data of Javet, Ibl and Hintermann (137) who observed an overpotential increase of approximately 200 mV at 1.38 A/dm^2 with 2.6 x 10^{-4} M thiourea and a disk electrode rotating at 1000 r.p.m.

Of interest, but not directly comparable to the above studies, are polarization measurements obtained in unstirred acid copper sulfate solutions that contained high concentrations of thiourea (0.013 to 0.13 M). The large overpotential increases were ascribed to an adsorbed layer of $[CuTu_3]^+$ on the electrode surface (138).

The discrepancies apparent in these data may be attributed, to some extent, to difficulties in measuring overpotentials (139-142), and to different values of the concentration polarization (143-146), but may be due largely to other factors such as preparation of the electrodes and the electrolyte (c.f. previous section on reactions during mixing of thiourea and acid copper sulfate) and the age of the solution (41).

Various workers have studied the occlusion of thiourea in copper electrodeposited from acid copper sulfate solutions containing thiourea. Using thiourea labelled with the isotopes ^{35}S or ^{14}C, Llopis et al (30) demonstrated cleavage of the thiourea molecule during the deposition process from unstirred electrolyte. Sulfur-35 was occluded in large quantities, whereas very little ^{14}C was found. The published data do not permit calculation of weight percent values of sulfur or carbon in the deposit. However, it was assumed that simple cleavage had occurred and that the sulfur was present in the form of sulfide. The cleavage of thiourea during copper electrodeposition was later confirmed by other investigators who also determined occlusion with thiourea-^{35}S and thiourea-^{14}C. (31,147).

Sutyagina studied occlusion in unstirred systems by determining sulfur in the deposit radiochemically with thiourea-^{35}S, and also by combustion analysis. At a current density of 1.4 A/dm^2 and for thiourea concentrations of 5.3×10^{-4} to 2.6×10^{-3} M, the radiotracer method gave sulfur contents of the deposits in the range 0.25 to 0.50 wt %, while chemical analyses indicated 0.15 to 0.37 wt % (148) At a higher current density (2.5 A/dm^2) with thiourea-^{35}S in unstirred acid copper sulfate solution at a temperature of 20°C, sulfur contents of deposited copper have been estimated radiochemically to be 0.17, 0.78, 1.16 and 2.01 wt % for bulk thiourea concentrations of 8.4×10^{-5}, 4.2×10^{-4}, 8.3×10^{-4} and 1.67×10^{-3} M, respectively (149). On the other hand, when Raub and Schiffner (38) determined the carbon and sulfur contents of copper deposited from unstirred solution by chemical methods (unspecified), for thiourea concentrations of 0.5×10^{-3} to 3×10^{-3} M and current densities from 0.25 to 2.0 A/dm^2, they found carbon in the deposits in such quantity (0.04 to 0.11 wt %) that they assumed occlusion in the copper of the cuprous-thiourea complex reported by Javet and Hintermann (37). The sulfur contents ranged from 0.06 to 0.28 wt %.

In contrast to the large S contents of deposits reported by other workers, Kolbasov et al (150) used thiourea-^{35}S and thiourea-^{14}C to show that the presence of 4×10^{-5} M thiourea at 2 A/dm^2 caused only 0.007 wt % sulfur to be occluded during electrodeposition of copper from unstirred acid copper sulfate solution.

With a rotating disk cathode and a thiourea concentration of 10^{-3} M, it has been demonstrated (36,39,151) that the incorporation of sulfur from thiourea-^{35}S is purely diffusion controlled at high current densities (> 1 A/dm^2) and values of $\omega^{\frac{1}{2}}.C_o$ (ω = angular velocity of disk electrode, C_o = bulk concentration of additive, mole cm^{-3}) up to 6×10^{-6} mole cm^{-3} sec^{-1}. At lower current densities and larger values of $\omega^{\frac{1}{2}}.C_o$, the process is no longer predominantly controlled by diffusion. Only trace amounts of carbon were occluded from thiourea-^{14}C, and the sulfur content (radiochemical) at 2 A/dm^2 ranged from 0.5 to 1.2 wt % for electrode rotational velocities of 330 to 1460 r.p.m. (36).

Barnes and Storey (152) claim that the presence of 5×10^{-8} to 10^{-5} M thiourea in acid copper sulfate solution has no effect on the structure of electrodeposited copper.

By contrast, Okada et al (153) found that 5.3 x 10^{-4} M thiourea in the electrolyte resulted in very fine-grained deposits with no development of a characteristic plane. This is supported by other observations that 6.6 x 10^{-5} M thiourea greatly modified the structure of electrodeposited copper (154-156).

Polukarov et al have demonstrated the presence of a large number of deformation and packing defects in copper deposited from acid copper sulfate solution containing thiourea (157). They attributed subsequent changes in the resistance and internal stress of the deposited copper to internal ordering phenomena (158-159).

EXPERIMENTAL AND RESULTS

Equipment

The electrolysis cell consisted of separate anode and cathode compartments joined by a 10 mm O.D. glass tube fitted with a medium porosity sintered glass disk (Figure 31). The compartments were sealed with Teflon covers provided with holes for the introduction of the electrodes, gas inlets and outlets, a Luggin-Haber capillary and a small glass bulb containing thiourea or formamidinedisulfide solution when desired. The covers were machined to a reasonably tight fit, so that a slight positive pressure of purified nitrogen could be maintained inside the cell for operation under relatively oxygen-free conditions.

The cathode was 0.010" copper foil (Fisher) backed by 1/16" copper sheet for support. It was placed in a recess in a Teflon holder that exposed an electrode area of 5.25 cm^2 to the electrolyte (Figure 32). Overpotential measurements were made against a saturated calomel reference electrode in a separate compartment designed to prevent diffusion of KCl into the test compartment during an experiment (up to 48 hrs). The Luggin-Haber probe had a tip of diameter less than 0.5 mm that rested lightly on the cathode surface. It was connected to the reference electrode compartment by 1/8" O.D. Teflon tubing filled with electrolyte of the test compartment. Potentials between the test electrode and the saturated calomel reference electrode were measured with an Orion 701 mV/pH meter. When necessary, the measured potential could be displayed on a Sargent SRG chart recorder. Currents were measured with a Tinsley type 4237 milliammeter, or by determining the potential drop across a standard resistor in series with the cell. Current was supplied by a 48 V bank of lead storage batteries and regulated by several high wattage variable resistors connected in series.

Materials

Deionized-distilled water was re-distilled in a Pyrex unit designed for continuous operation. This was

FIGURE 31

SCHEMATIC DIAGRAM OF THE TWO COMPARTMENT ELECTROLYSIS CELL

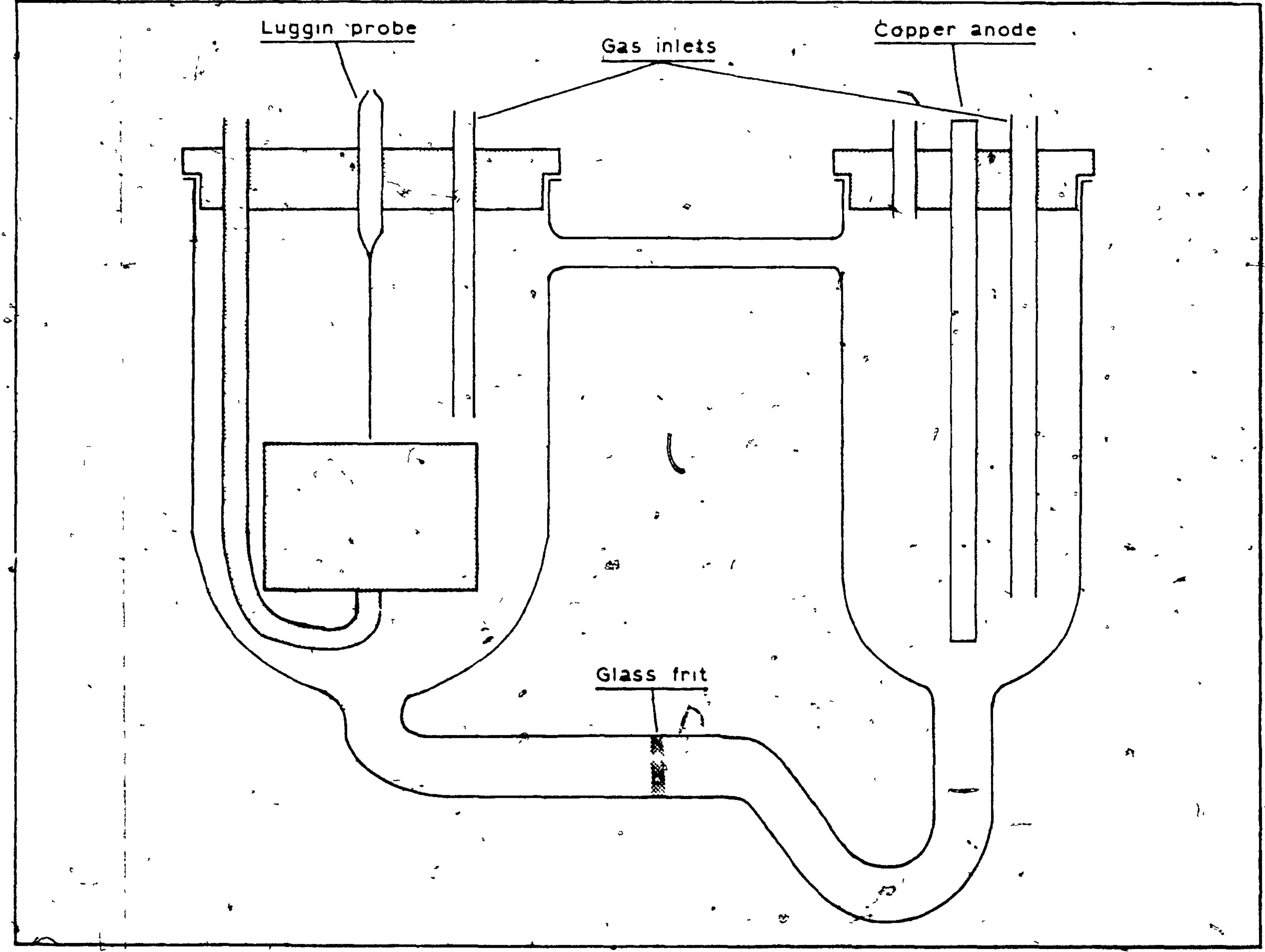
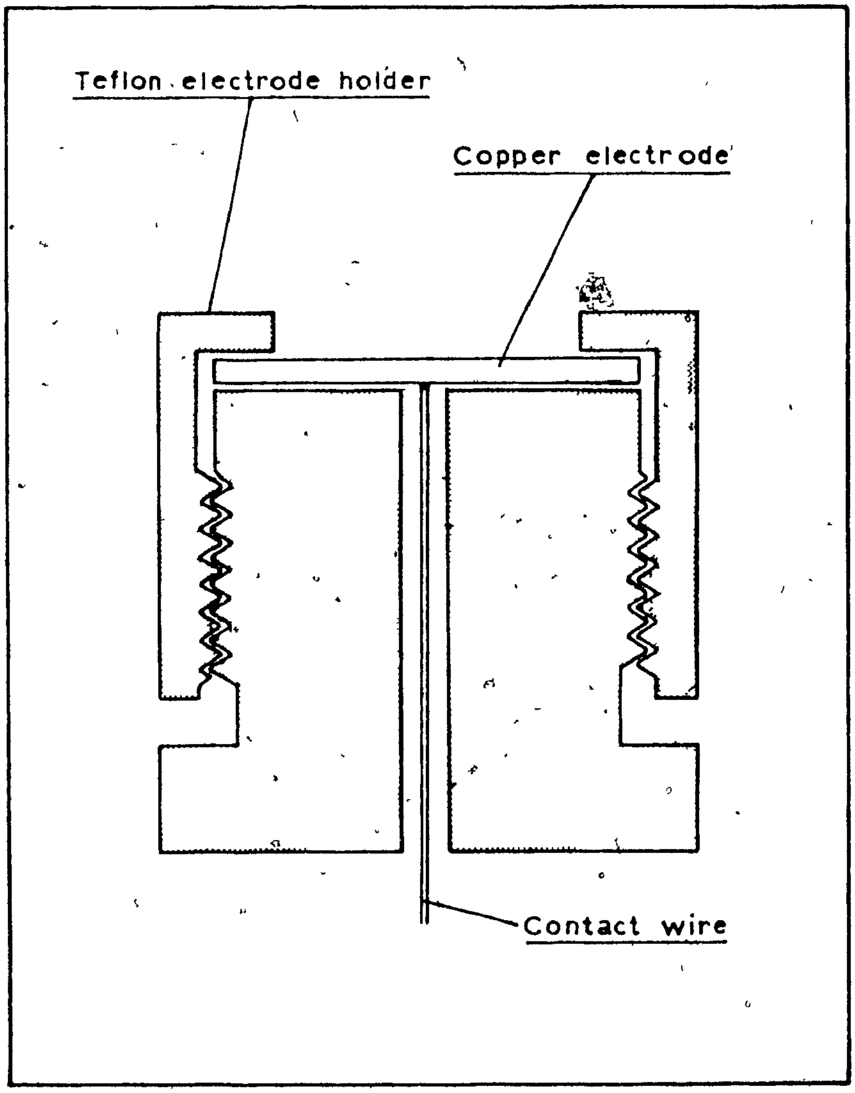

Luggin probe
Gas inlets
Copper anode
Glass frit

FIGURE 32

SCHEMATIC DIAGRAM OF THE CROSS-SECTION OF THE TEFLON ELECTRODE HOLDER USED IN THE PRESENT INVESTIGATION


Teflon electrode holder
Copper electrode
Contact wire

followed by one slow distillation from alkaline permanganate and one further distillation to ensure minimum contamination by $KMnO_4$ that might have been carried over in the preceding operation. Sulfuric acid (Anachemia, 96%, reagent grade) was distilled in Pyrex equipment at atmospheric pressure. Copper sulfate pentahydrate (Fisher, certified reagent) was recrystallized three times from water that had been purified as above, and made slightly acidic. Hydrogen peroxide (1.0 ml/l, Fisher, certified reagent, 30%) was added to the hot solution during the second recrystallization to minimize residual levels of possible organic surface-active substances. Excess peroxide was then destroyed by prolonged heating at 80-90°C. The hot solutions were filtered by suction through glass fibre filters (Reeve Angel) supported on a medium porosity sintered glass filter. Thiourea (Baker analyzed reagent) was used as supplied. Formamidinedisulfide sulfate monohydrate was freshly prepared by hydrogen peroxide oxidation of thiourea, as described previously.

The copper foil cathodes were treated with hot concentrated sodium hydroxide solution, followed by distilled water and acetone (Eastman, spectrograde) to remove grease. They were then etched for 10-15 seconds in 8M H_2SO_4, 1M HNO_3. Anodes were ¼" electrolytic copper rod (Drummond and McCall) cleaned before each experiment by the same procedure as that used for the cathodes.

CURRENT EFFICIENCY FOR COPPER ELECTRODEPOSITION FROM ACID COPPER SULFATE SOLUTION

Before the effects of thiourea and its oxidation product, formamidinedisulfide, on the electrodeposition of copper could be assessed, it was necessary to determine the behaviour of the system in the absence of these additives, i.e., in the pure standard electrolyte, which consisted, as previously, of 0.50 M $CuSO_4$ in 1.00 M H_2SO_4 solution.

Experiments with a vertical cathode indicated that the current density distribution was uneven when the current was large enough to cause significant convection currents, while a horizontal cathode facing downwards caused depletion of the electrolyte at the electrode surface and subsequent hydrogen evolution, even at current densities as low as 0.5 A/dm^2. On the other hand, the limiting current density for copper deposition with a horizontal cathode facing upward was approximately 9A/dm^2, and the current density appeared to be quite uniform over the whole cathode area. This was indicated by the uniform thickness of copper deposited over the surface at 2.0 and 6.0 A/dm^2 after prolonged electrolysis (up to 1 mm thick deposit).

The current efficiency for copper deposition was determined, both in the presence and absence of atmospheric oxygen, to ensure that formation of metallic copper was the main process in the current density range considered. The number of coulombs passed was determined either by a silver coulometer (160) or as the product of current and time. The constant current was measured as the potential drop across a calibrated 23.15 ohm resistor with a DANA digital voltmeter. Both methods gave current efficiencies of 98 to 100% for current densities from 0.02 to 6.0 A/dm^2 (Table 25, Figure 33). It might be noted that the addition of thiourea to the standard electrolyte to a concentration of 10^{-3} M did not cause a significant change in the current efficiency.

POLARIZATION OF COPPER ELECTRODES IN PURE ACID COPPER SULFATE SOLUTION

Polarization measurements were made in the two compartment cell shown schematically in Figure 31. In the first experiments, a reference electrode of electroplated copper wire in pure standard electrolyte was employed. However, values of the rest potential of one reference electrode measured against a presumably identical electrode were found to vary over a range from + 4 to -9 mV, probably because of differences in strain and corrosion potentials. The rest potentials of copper electrodes in the standard electrolyte were also found to change when the solution was stirred, with random fluctuations over a range of about 2 mV. This fluctuation probably results from corrosion currents in establishing the equilibrium

$$Cu^{0} + Cu^{2+}_{aq} = 2Cu^{+}_{aq}$$

TABLE 25

CURRENT EFFICIENCY FOR ELECTRODEPOSITION OF COPPER FROM STANDARD ELECTROLYTE AT 25°C*

Current Density A/dm^2	Charge Passed Coulombs	wt of Deposit g	Current Efficiency %
0.0076	1078[b]	0.2811	79.2
0.014	1233[b]	0.3300	82.0
0.058	775[b]	0.2452	96.1
0.145	1583[b]	0.5089	97.7
0.146[a]	1085[b]	0.3495	97.8
0.294	629[b]	0.2022	97.6
0.295[a]	465[b]	0.1488	97.1
0.581[a]	1552[b]	0.5061	99.0
0.589	694[b]	0.2264	99.1
1.14[a]	672[b]	0.2183	98.6
1.17	367[b]	0.1201	99.5
1.72	554[b]	0.1795	98.4
1.73[a]	763[b]	0.2486	99.0
2.78[a]	741[b]	0.2405	98.6
2.81	606[b]	0.1981	99.2
4.16	808[b]	0.2651	99.6
6.04	648[b]	0.2111	98.9
1.05	734[c]	0.2377	98.3
1.93	744[c]	0.2439	99.5
3.02	566[c]	0.1850	99.2
6.03	657[c]	0.2158	99.8
1.44[d]	756[b]	0.2481	99.6
2.55[d]	692[b]	0.2255	99.0
2.57[d]	653[b]	0.2128	98.9
5.41[d]	574[b]	0.1869	98.9

*

a - deposition under nitrogen atmosphere

b - number of coulombs determined as I x t

c - number of coulombs determined with silver nitrate coulometer

d - deposition from standard electrolyte containing 10^{-3} M thiourea

Since copper reference electrodes were found to be unsatisfactory, they were abandoned in favor of a saturated calomel reference electrode (Fisher, cracked bead type). The relatively small, reproducible liquid junction potential encountered in using a saturated calomel reference was judged preferable to the instability of a copper reference, particularly since a liquid junction potential should be largely or completely eliminated in the relative determination of overpotential differences in the absence and presence of the addition agent. When a constant current was impressed on a freshly etched copper cathode in the standard electrolyte, the overpotential changed with time and rapidly approached a steady state value after about 5 to 10 minutes (Figure 34).However, when the current was passed through a cathode electodeposited at a similar current density a steady state value was achieved within one or two minutes. Momentary potential maxima were sometimes observed when the current was switched on, but the steady state polarization achieved thereafter was the same as when no such maxima were observed. The value of the steady state polarization was reduced slightly by stirring, which reduced the concentration polarization. This could presumably be best achieved with a rotating disk electrode with a constant angular velocity, but this elaboration was not considered necessary in the present study.

All the polarization values used for Tafel plots of

FIGURE 33

CURRENT EFFICIENCY FOR COPPER ELECTRODEPOSITION FROM STANDARD ELECTROLYTE AT 25°C

+ deposition under nitrogen atmosphere

o deposition in presence of atmospheric oxygen

● deposition from solution containing 10^{-3} $\underline{M}$ thiourea

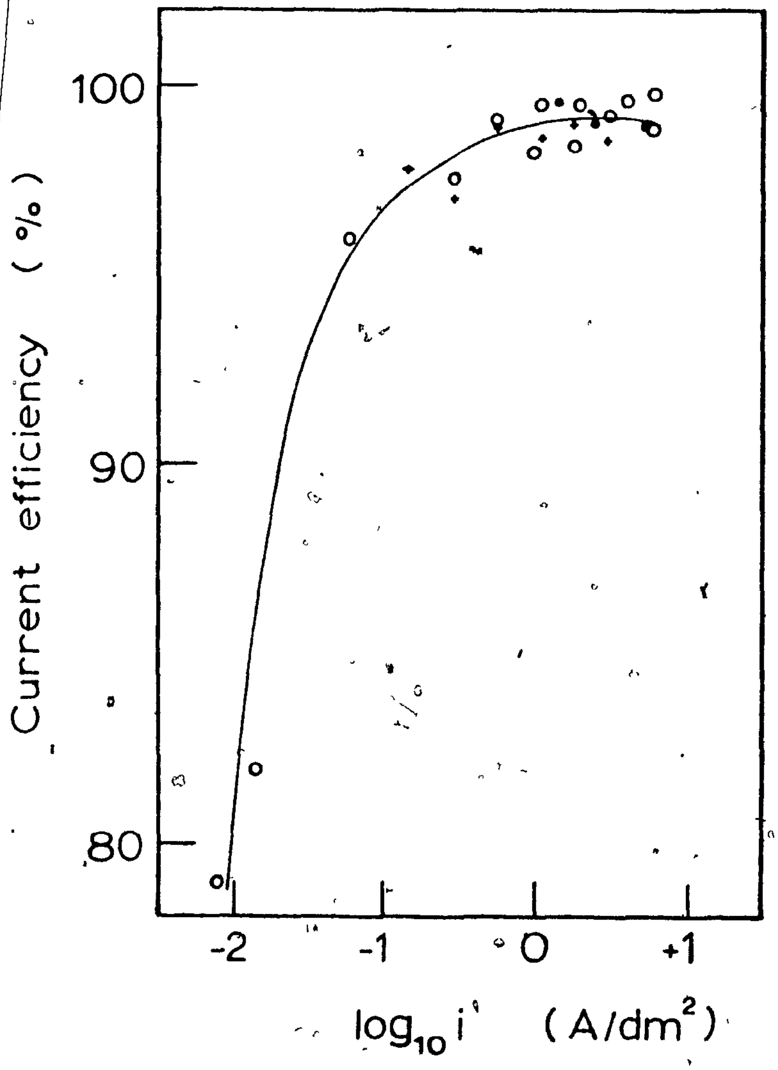
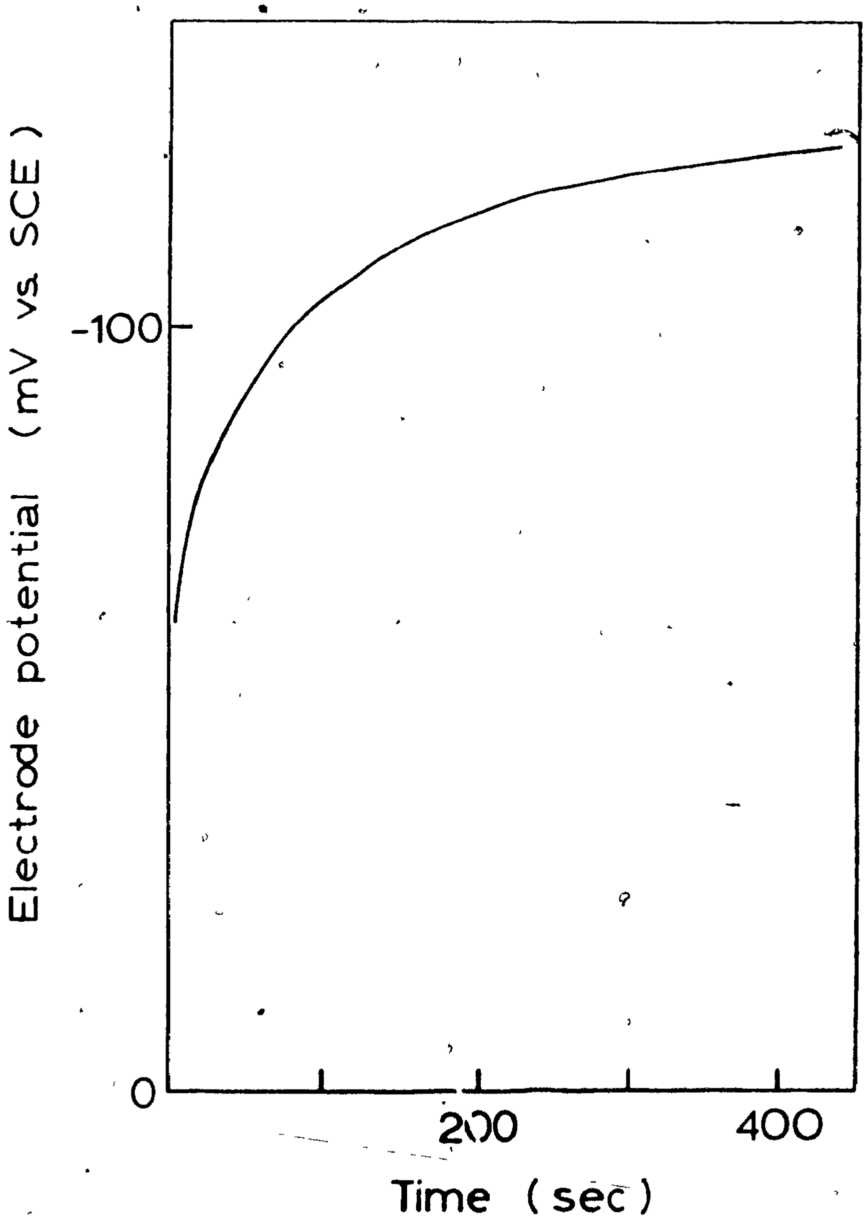

Current efficiency (%)
100
90
80
-2
-1
0
+1
log10 i (A/dm2)

FIGURE 34

CHANGE IN OVERPOTENTIAL WITH TIME FOR A FRESHLY ETCHED COPPER CATHODE IN STIRRED PURE STANDARD ELECTROLYTE AT A CONSTANT CURRENT DENSITY OF 4.17 A/dm^2, WITH A TEMPERATURE OF 25°C AND IN A NITROGEN ATMOSPHERE


Electrode potential (mV vs SCE)
-100
0
200
400
Time (sec)

overpotential (η) against the logarithm of the current density (log i) are reported as steady state values for the given conditions. The measured cathode overpotentials are summarized in Table 26 and the corresponding anode polarizations are found in Table 27. The exchange current densities and Tafel slopes are estimated from the linear portions of the graphs which were drawn without recourse to the least-squares method.

The results of the polarization measurements are in good agreement with those of other workers, and it may therefore be assumed that the polarization cell and its ancillary equipment functioned adequately.

Microscopic examination of the copper deposited from purified standard electrolyte indicated large block crystals at current densities less than 2 A/dm^2. Cross-sections of the deposits confirmed the presence of large grains with no superimposed structural features such as columns or layers. With increase of current density, the deposits became increasingly finer crystalline, and finally nodular in appearance.

POLARIZATION OF COPPER IN ACID COPPER SULFATE SOLUTIONS CONTAINING THIOUREA

Thiourea added to the standard electrolyte caused only a slight change (< 5 mV) in the rest potential of a copper electrode immersed in the solution, but the change in overpotential when current was passed through a copper

TABLE 26

SUMMARY OF PARAMETERS OBTAINED FROM TAFEL PLOTS FOR THE CATHODIC POLARIZATION OF COPPER IN STANDARD ELECTROLYTE AT 25°C*

Exchange current density (A/dm^2)	Tafel Slope (mV/decade current)
0.246	113^a
0.279	131^a
0.360	167^a
0.275	130^a
0.182	90^a
0.228	89^a
0.250	88^a
0.229	98^a
0.286	98^b
0.290	100^b
0.335	103^b
0.202	92^c
0.197	113^c
0.216	124^c

* a - unstirred electrolyte under nitrogen
b - stirred electrolyte under nitrogen
c - unstirred electrolyte, air saturated

The average overpotential at 2.0 A/dm^2 was 105 ± 9 mV.

TABLE 27

SUMMARY OF PARAMETERS OBTAINED FROM TAFEL PLOTS FOR THE ANODIC POLARIZATION OF COPPER IN STANDARD ELECTROLYTE AT 25°C *

Exchange current density (A/dm^2)	Tafel Slope (mV/decade current)
0.243	29[a]
0.203	26[a]
0.224	27[a]
0.277	17[b]
0.298	18[b]
0.284	18[b]

* a - unstirred electrolyte under nitrogen

b - stirred electrolyte under nitrogen

electrode immersed in the solution was much more pronounced.

When the steady state potential had been attained at a freshly etched copper cathode in stirred, pure standard electrolyte at 2.74 a/dm^2, a small glass bulb containing thiourea in aqueous solution (14.3 mg thiourea in 2.0 ml H_2O) was broken in the electrolyte, to bring the thiourea concentration in the cathode compartment to 1.0 x 10^{-3} M. The cathode polarization increased immediately and reached a new plateau value within 15 seconds (Figure 35). This overpotential was maintained during two hours. This would seem to indicate that the steady state effect of thiourea on the electrodeposition process is established very rapidly.

In view of the many published investigations dealing with the effects of low concentrations ($\leq 10^{-4}$ M) of thiourea on the overpotential for copper electrodeposition, it seemed promising to try a more general approach in an attempt to understand the system. It was decided to investigate the effect of thiourea at concentrations higher than 10^{-3} M on the electrodeposition process. The effect of each concentration of thiourea on the deposition* was studied at current

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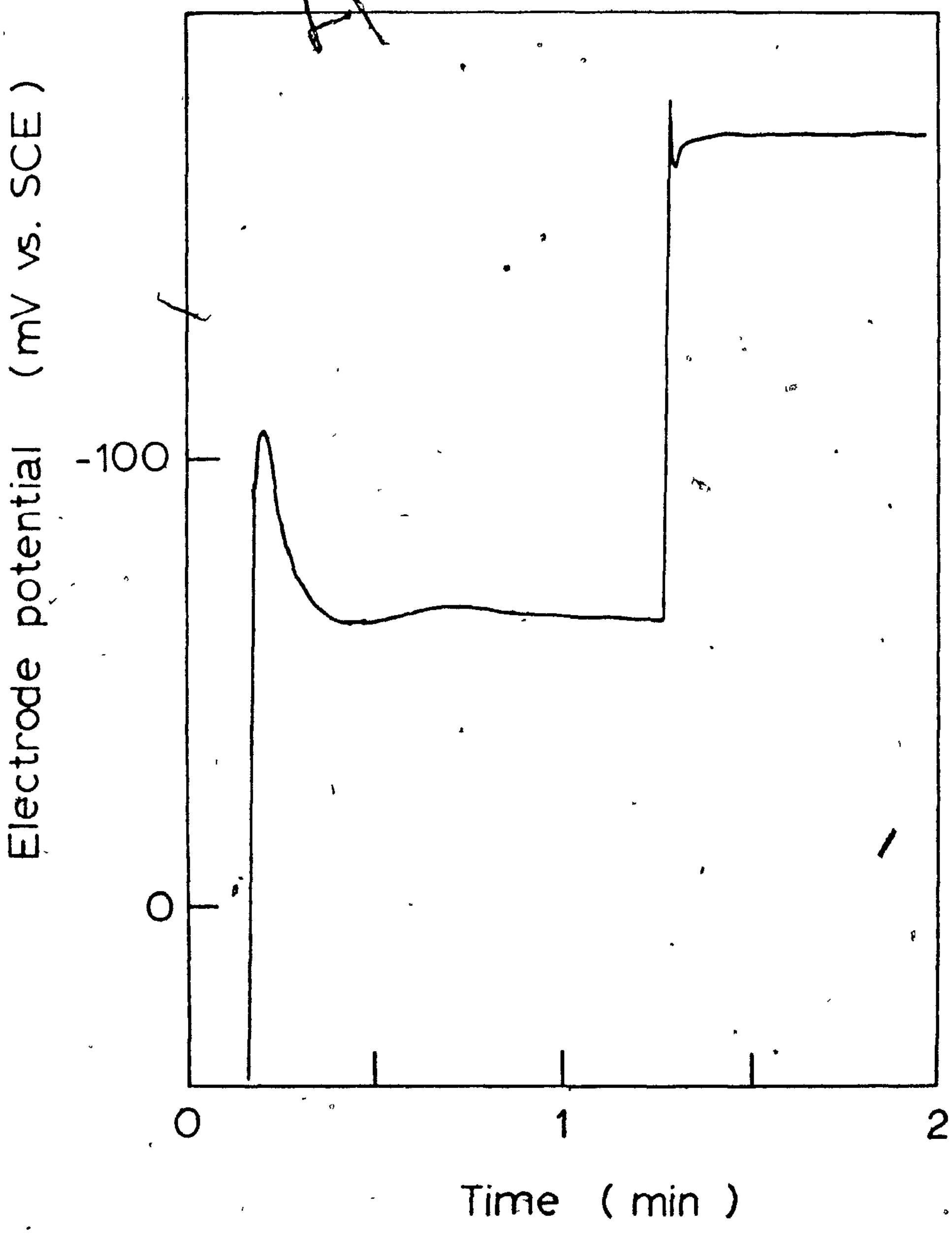
* Several experiments were made at each concentration of additive. The overpotentials were reproducible to ± 20 mV, but did not give linear Tafel plots. Reflectance values were also quite reproducible, but the effect of stress on the deposit (i.e. peeling as in Figure 38 or disintegration into flakes as in Figure 39) did not manifest itself in a very reproducible manner for

FIGURE 35

CHANGE IN CATHODE OVERPOTENTIAL AT 2.74 A/dm^2 CAUSED BY ADDING THIOUREA (14.3 mg/2 ml WATER) TO STIRRED STANDARD ELECTROLYTE (190 ml) AT 25°C


Electrode potential (mV vs. SCE)
-100
0
0
1
2
Time (min)

densities of 0.8, 4.0 and 8.0 A/dm^2 which were chosen as representative of low, average and high current densities respectively.

Where mechanical stability of the deposits permitted, the relative specular reflectance of the deposit was determined with a photocell (National Semiconductors Ltd., Type NSL 703) in the apparatus (c.f. refs. 29, 161, 162) schematically depicted in Figure 36. The reflectances were measured relative to a silvered glass mirror, to which was assigned an arbitrary value of 100% reflectance.

The deposits obtained from standard electrolyte containing 0.05 M thiourea in an unstirred solution (Figure 37) were very highly stressed at current densities of 8.0 and 4.0 A/dm^2. This was apparent from the spontaneous detachment of parts of the deposit from the substrate. These deposits contained thick black areas and thinner films that showed blue-green interference patterns, possibly due to sulfide. Other areas contained a fine network of white crystals (Figure 38) which, after treatment with nitric acid,

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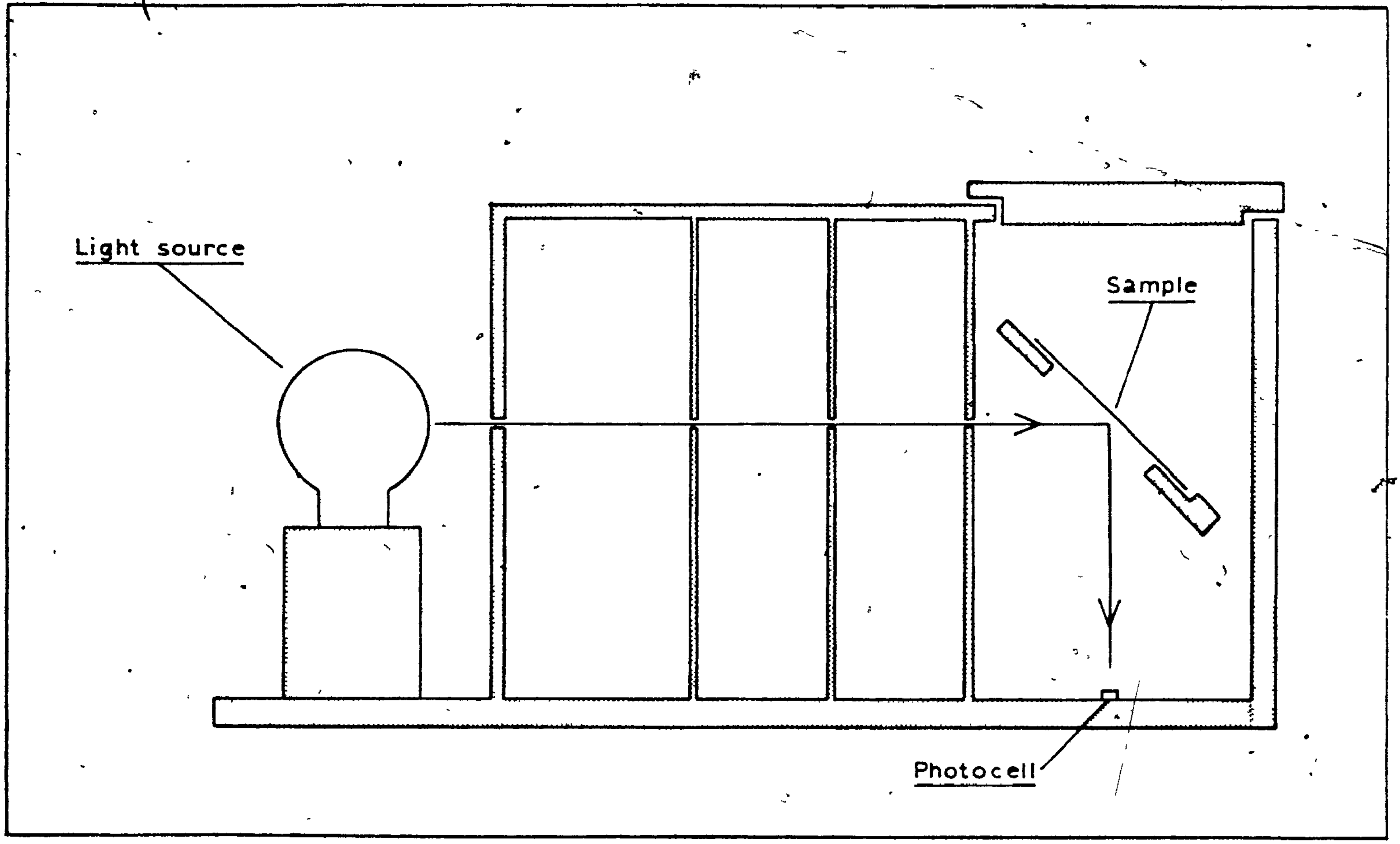
deposits obtained under presumably identical conditions. Thus, some deposits peeled during deposition, while others, under the same conditions, did so only after some time had passed. However, the net result was the same, and the deposits shown and described are representative samples.

FIGURE 36

APPARATUS USED FOR DETERMINING RELATIVE REFLECTANCE VALUES FOR ELECTRODEPOSITED COPPER



Light source
Sample
Photocell

FIGURE 37

TOP PHOTOGRAPH*

DEPOSITS FROM STANDARD ELECTROLYTE CONTAINING
0.05 M THIOUREA

BOTTOM PHOTOGRAPH

DEPOSITS FROM STANDARD ELECTROLYTE CONTAINING
0.05 M FORMAMIDINEDISULFIDE SULFATE MONOHYDRATE

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* The bottom row in each photograph represents the corresponding deposits from standard electrolyte containing 0.001 M thiourea. Current densities for deposition were 0.8, 4.0 and 8.0 A/dm^2, respectively, from left to right.

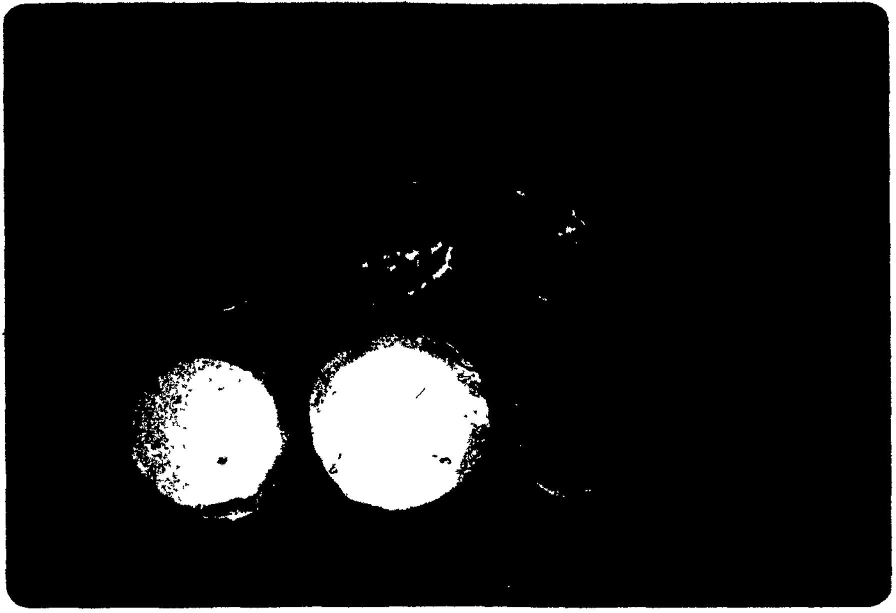


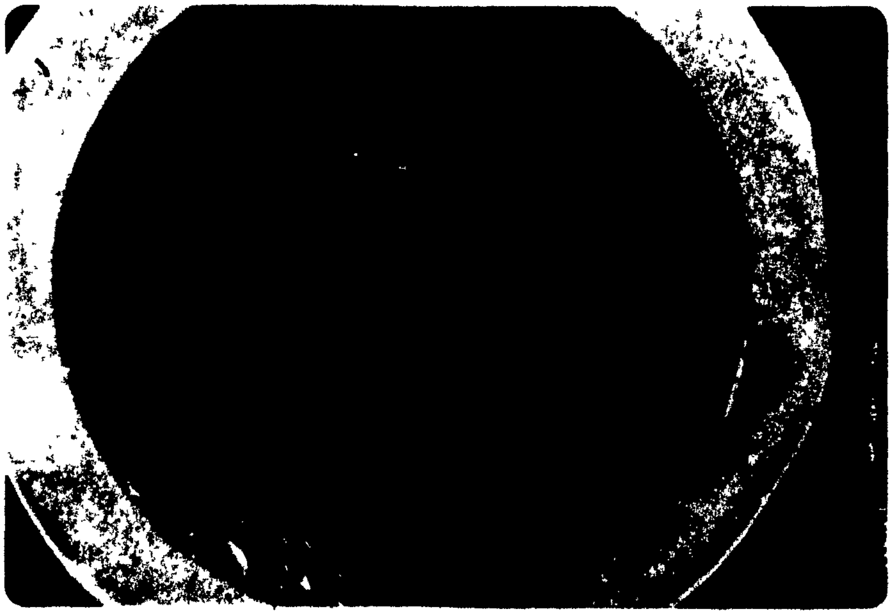
FIGURE 38

TOP PHOTOGRAPH

DEPOSIT AT 4 A/dm^2 FROM UNSTIRRED STANDARD ELECTROLYTE CONTAINING 0.05 M THIOUREA.
MAGNIFICATION, x 3.5

BOTTOM PHOTOGRAPH

DEPOSIT AT 4 A/dm^2 FROM UNSTIRRED STANDARD ELECTROLYTE CONTAINING 0.01 M THIOUREA.
MAGNIFICATION, x 3.5



gave a positive test for copper. The deposit at 0.8 A/dm^2 appeared to consist mainly of a mixture of a black substance, probably copper sulfide*, and relatively large, well-formed needles, presumably cuprous-thiourea sulfate complexes.

In contrast to this, the presence of 0.05 M formamidinedisulfide sulfate monohydrate in the standard electrolyte did not show any effect on the deposit at current densities of 0.8 and 4.0 A/dm^2. However, at 8 A/dm^2 the deposit was evenly blackened, again attributable to a film of copper sulfide (Figure 37).

The overpotentials with the formamidinedisulfide additive were higher than those with pure standard electrolyte, but less than those measured in a solution containing an equal concentration (0.05 M) of thiourea. At 0.8 A/dm^2, the electrode potential in the presence of 0.05 M thiourea was -310 to -320 mV, whereas, for 0.05 M formamidinedisulfide, it was -150 to -160 mV. This would seem to be a case where increased polarization is not accompanied by brightening or levelling.

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* Similar black areas were noted in many of the deposits to be described, and will henceforth be ascribed to copper sulfide since they were subsequently identified to contain the sulfide ion.

The effect of stirring the solutions (0.01 M thiourea) was to give brighter, but more highly stressed deposits (Figure 39). Dark patterns on the deposit at 4 A/dm^2 (Figure 38) from unstirred solution were presumably areas of various copper sulfide contents, caused by depletion and enrichment of thiourea in the vicinity of the cathode by convection currents. Microscopic examination of the surface showed many small cracks and some small needles that resembled trithioureadicuprous sulfate monohydrate (Figure 40). The deposit was highly stressed, and after one hour, it was reduced to a mass of small, brittle flakes (Figure 39). Although the complex appeared to be the same as that described earlier (trithioureadicuprous sulfate monohydrate, Figure 40) it might have been a new complex of cuprous sulfate with thiourea.

At 8 A/dm^2 and 0.01 M thiourea, the deposit had a dull copper color and contained a network of very fine cracks (Figure 41). At one-tenth the current density (0.8 A/dm^2) there were fewer cracks, but the deposit showed black areas of copper sulfide and very fine, white networks of complex lying in cracks in the deposit (Figure 42).

When the thiourea concentration was reduced to 5.3×10^{-4} M with a current density of 4 A/dm^2, the structure of the deposit had not suffered modification and the deposit obtained (Figure 43) resembled that obtained from

FIGURE 39

TOP PHOTOGRAPH*

DEPOSITS FROM STIRRED STANDARD ELECTROLYTE CONTAINING 0.01 M THIOUREA

BOTTOM PHOTOGRAPH

DEPOSITS FROM UNSTIRRED STANDARD ELECTROLYTE CONTAINING 0.01 M THIOUREA

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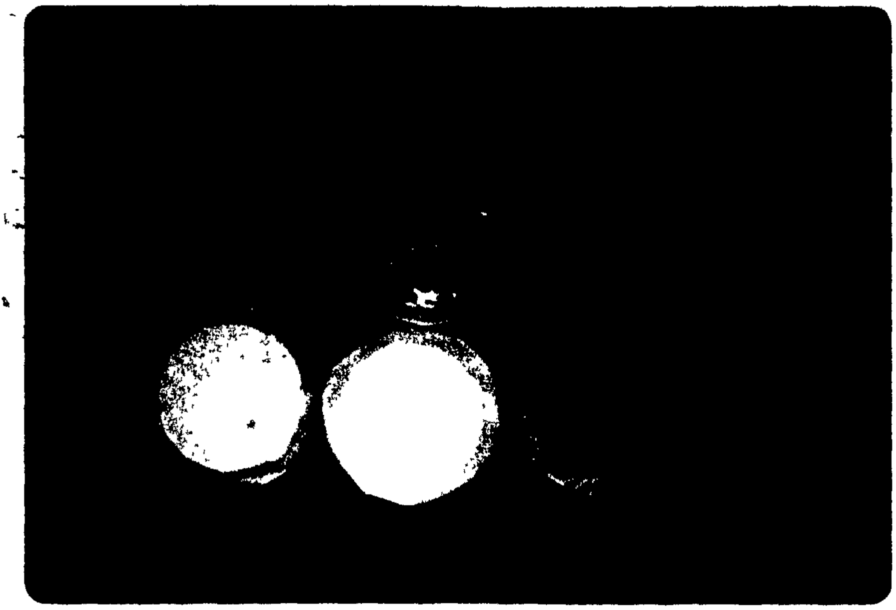
* The bottom row in each photograph represents the corresponding deposits from standard electrolyte containing 0.001 M Thiourea. Current densities for deposition were 0.8, 4.0 and 8.0 A/dm^2 respectively, from left to right.



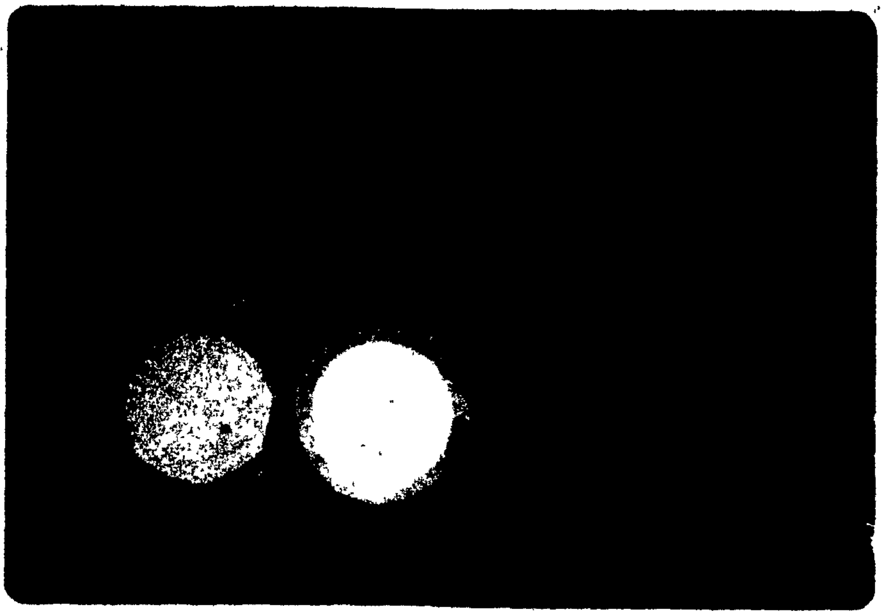


FIGURE 40

TOP PHOTOGRAPH

CRYSTALS OF $Cu_2Tu_3SO_4.H_2O$

MAGNIFICATION, x 100

BOTTOM PHOTOGRAPH

CRYSTAL ON SURFACE OF COPPER ELECTRODEPOSITED AT 4 A/dm^2 FROM STANDARD ELECTROLYTE CONTAINING 0.01 M THIOUREA

MAGNIFICATION, x 400

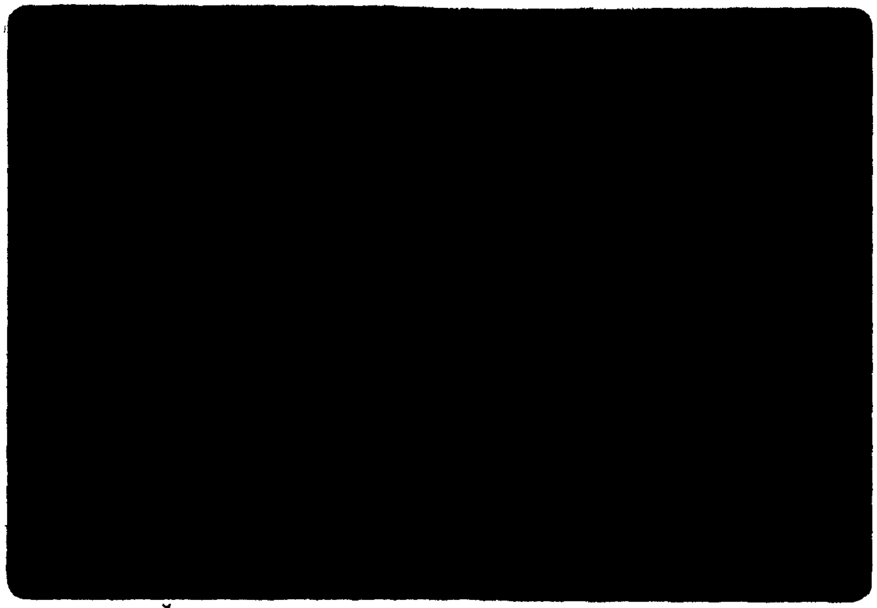


FIGURE 41

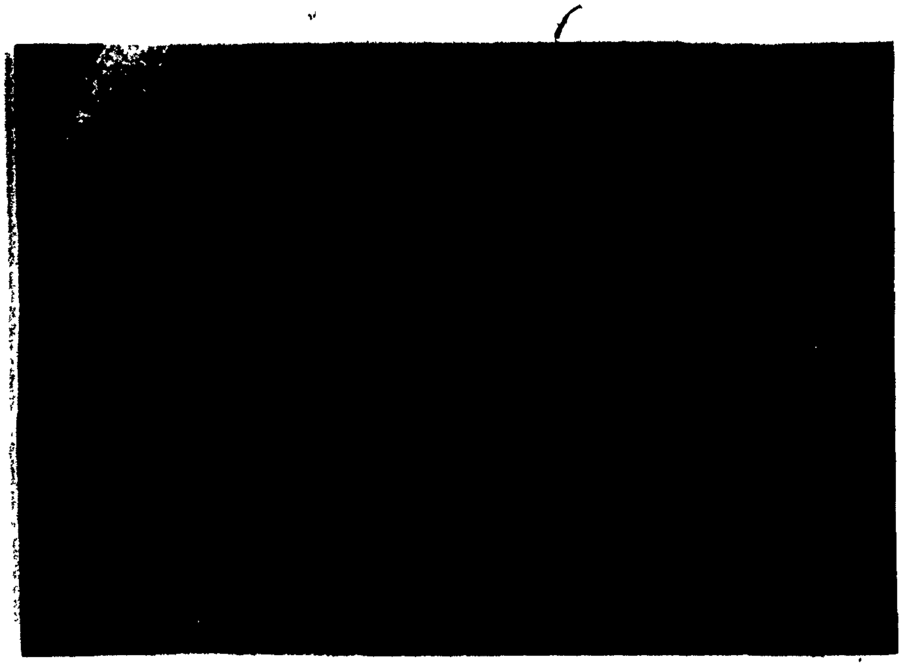
DEPOSIT OBTAINED AT 8 A/dm^2 FROM UNSTIRRED STANDARD ELECTROLYTE CONTAINING 0.01 M THIOUREA

TOP PHOTOGRAPH

MAGNIFICATION, x 3.5

BOTTOM PHOTOGRAPH

MAGNIFICATION, x 200



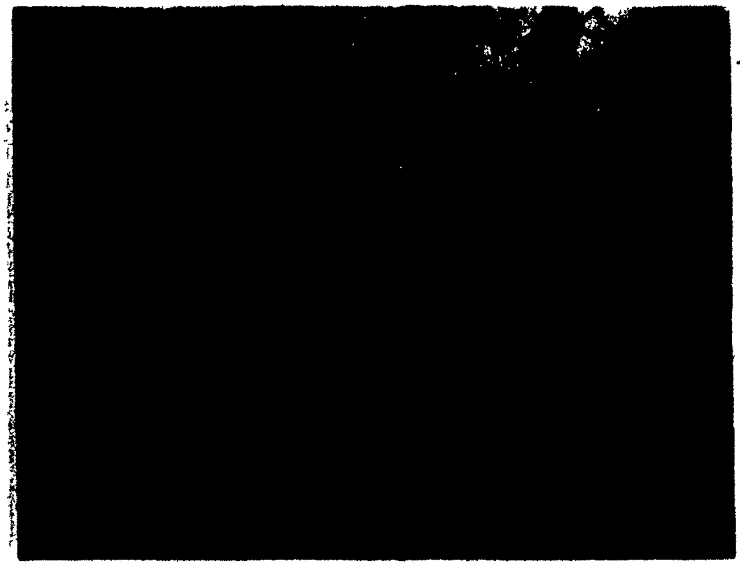


FIGURE 42

DEPOSIT OBTAINED AT 0.8 A/dm^2 FROM STIRRED STANDARD ELECTROLYTE CONTAINING 0.01 M THIOUREA

TOP PHOTOGRAPH

MAGNIFICATION, x 3.5

BOTTOM PHOTOGRAPH

MAGNIFICATION, x 400

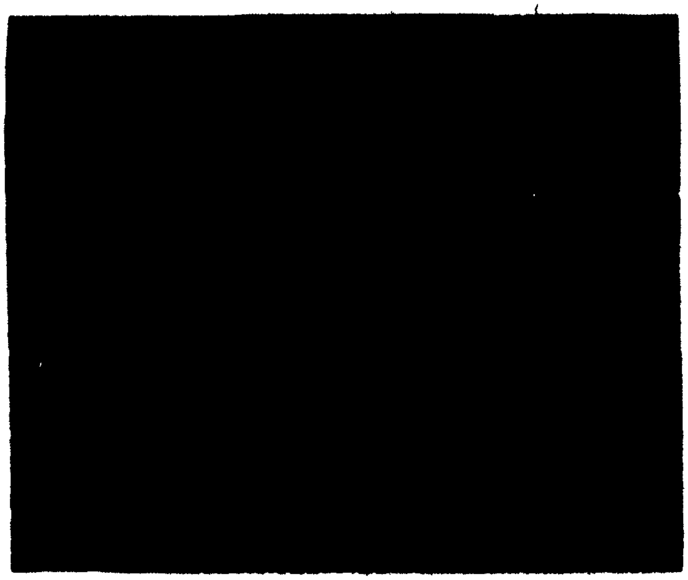


FIGURE 43

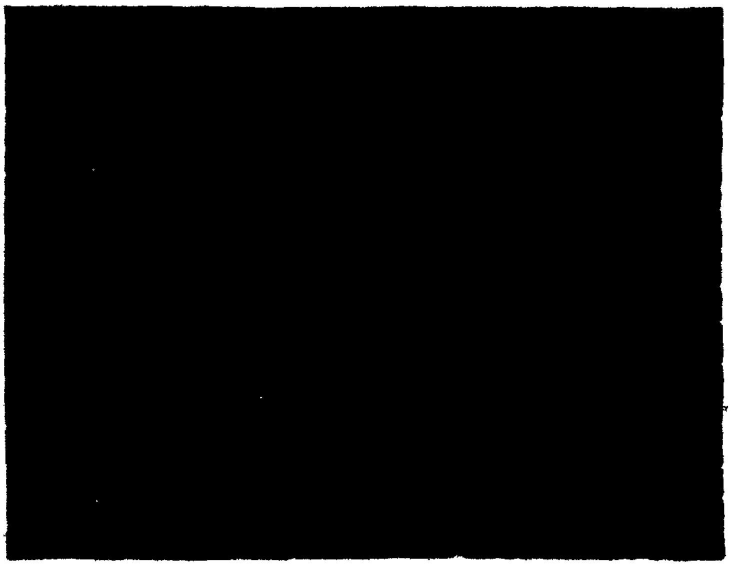
DEPOSIT OBTAINED AT 4 A/dm^2 FROM UNSTIRRED STANDARD ELECTROLYTE CONTAINING 0.00053 M THIOUREA

TOP PHOTOGRAPH

MAGNIFICATION, x 3.5

BOTTOM PHOTOGRAPH

MAGNIFICATION, x 200



pure standard electrolyte.

At thiourea concentrations of 0.1 and 0.05 M, and a current density of $4A/dm^2$, the copper appeared to be deposited in successive layers. Areas of black copper sulfide on the electrode spread at observable rates, and were then covered by spreading sheets of metallic copper which, in turn, were covered by advancing films of sulfide. This periodic phenomenon was accompanied by some hydrogen evolution. The spreading directions of the layers of copper and sulfide were strongly influenced by movement of the electrolyte. Diffusion control appeared, therefore, to be important in this phenomenon.

The process was recorded on 8mm film, but no quantitative measurements of overpotential or current efficiency were attempted. The rate of the redox reaction between thiourea and cupric ions was so high that precipitation of large amounts of trithioureadicuprous sulfate monohydrate occurred within two minutes of adding the thiourea solution. Such rapid change in the composition of the bulk solution made it unlikely that reproducibility could be achieved in mixing the solutions. In any event, it would have been impossible to relate the sequence of layers with any precision to the reactions that occurred in the solution.

Steady state polarization data and specular reflectance of the deposits are summarized in Table 28. The

TABLE 28

STEADY STATE POLARIZATION AND RELATIVE SPECULAR REFLECTANCE FOR COPPER DEPOSITED FROM STANDARD ELECTROLYTE CONTAINING THIOUREA AT 25°C.

[Tu] (M)	i (A/dm²)	Electrode potential mV vs SCE	Δη mV	Reflectance %
0	0.8	+ 8	0	14
0	4.0	-150	0	11
0	8.0	-230	0	6
0.05	0.8	-310	320	black
	4.0	(-440)	290	peeled
	8.0	(-540)	310	peeled
0.01	0.8	-210	220	22
	4.0	-390	240	77
	6.0	-350	-	22
	8.0	-370	240	4
0.01 stirred	0.8	-250	260	unstable
	4.0	-310	160	unstable
	8.0	-370	240	unstable
0.005	0.8	-210	220	46
	4.0	-320	170	61
	8.0	-550	320	3
0.001	0.8	-160	170	8
	4.0	-420	270	16
	8.0	-520	290	2
0.001 stirred	0.8	-150	160	16
	4.0	-240	90	22
	8.0	-350	120	9
0.00053 stirred	4.0	-240	90	32
0.000053	4.0	-160	10	22

overpotential increase caused by thiourea became smaller as its concentration was decreased, and almost disappeared at 5×10^{-5} M thiourea.

In view of the apparent deposition in layers described above, the cross-section of a deposit obtained in the presence of thiourea was studied to determine whether it might reveal a layered structure. Two deposits obtained in the presence of 10^{-3} M thiourea, at 4.0 and 6.0 A/dm^2, respectively, were sectioned, embedded in plastic and polished by standard metallurgical techniques. After etching with acid ferric chloride in 50% ethanol, the deposit at 4 A/dm^2 showed a complex structure with visible layering and internal cracks and occlusions, whereas the deposit at 6 A/dm^2 did not (Figure 44). An estimate of the sulfur content of the deposits was then made in an attempt to assess the extent to which disruption of the copper crystal lattice might be caused by occluded additive.

DETERMINATION OF THE SULFUR CONTENT OF COPPER ELECTRODEPOSITED FROM ACID COPPER SULFATE SOLUTION CONTAINING THIOUREA

The sulfur content of copper electrodeposited from acid copper sulfate solutions containing thiourea is generally quite small, and sensitive analytical techniques are required for its estimation. Hitherto, the thiourea molecule has usually been labelled with the radioactive sulfur isotope ^{35}S, and the amount of sulfur in a solution

FIGURE 44

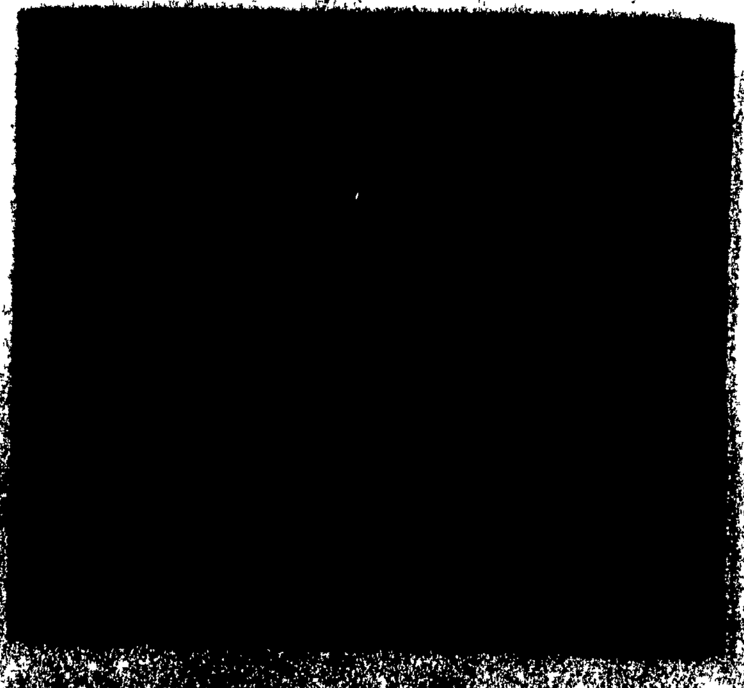
CROSS-SECTIONS OF COPPER DEPOSITED FROM STANDARD ELECTROLYTE CONTAINING 10^{-3} M THIOUREA

TOP PHOTOGRAPH

4 A/dm^2, MAGNIFICATION, x 600

BOTTOM PHOTOGRAPH

6 A/dm^2, MAGNIFICATION, x 400



of the copper deposit determined by either direct or liquid scintillation counting techniques. A high specific activity ($\geq$ 0.5 mC l^{-1}) is required for accurate results.

In the present investigation, it was desired to determine not only the quantity, but also the chemical form of the sulfur occluded in the deposit. It was decided, therefore, to maximize the sulfur content by working with high thiourea concentrations and low current densities, and to apply chemical methods to the larger quantities of sulfur compounds then available in the deposit for identifying the chemical state and estimating the amount present. The amount of sulfur occluded in the deposit as sulfate ions from the electrolyte has been reported to be extremely low (163) and no attempt was made to distinguish it from the sulfur occluded from other sources.

The method devised by Bartolacini and Barney (164,165) for the colorimetric determination of sulfate with barium chloranilate was used to determine the amount of sulfur occluded in the deposit. The method is based on the reaction

$$Y^{-} + MA\ (\text{solid}) \rightarrow A^{-} + MY\ (\text{solid})$$

where Y^{-} is the anion to be determined and A^{-} is a colored anion of an organic acid. MY must be so much less soluble than MA that the reaction is quantitative, while MA must be only sparingly soluble, so that blanks in A^{-} will not be too high.

The reaction of slightly soluble barium chloranilate with sulfate ion in acid solution of pH ~ 5 is used to give barium sulfate and the acid-chloranilate ion

$$SO_4^{=} + BaC_6Cl_2O_4 + H^+ \rightarrow H\,C_6Cl_2O_4^- + BaSO_4$$

The amount of acid chloranilate liberated is proportional to the sulfate ion concentration. The reaction is conducted in 50% aqueous ethyl alcohol buffered at an apparent pH of approximately 5. The presence of ethyl alcohol increases the sensitivity of the method by decreasing the solubilities of barium sulfate and barium chloranilate. Sodium and ammonium ions do not interfere at the 250 ppm level, but other cations must be removed by ion exchange. Chloride and nitrate ions are said not to interfere at the 100 ppm level. Using the 332 nm peak of the acid chloranilate ion, the spectrophotometric limit of detection in 10 mm cells was about 2 µg of sulfur (≈ 6 µg SO_4).

Barium chloranilate (Eastman) was purified from residual chloranilic acid by Soxhlet extraction with 95% ethanol for three days. The pH dependence of the absorbance at 332 nm indicated that pH ~ 5 was the lower limit for satisfactory behaviour (Table 29, Figure 45). A calibration curve was prepared with standard sodium sulfate solution. A linear plot was obtained of absorbance against amount of sulfur present, as sulfate, over the range 6.70 µg to 200 µg sulfur in 10 mm cells, and up to 2.00 mg sulfur using 1 mm cells. (Table 30, Figure 46).

To obtain samples of electrodeposited copper, a platinum foil cathode was placed in the two-compartment cell used for polarization studies, and copper deposited on it from standard electrolyte without, or with thiourea added. The deposit (200 ± 5 mg) was dissolved in concentrated, distilled nitric acid (1.00 ml) by gentle heating. The resulting solution was brought to pH ~ 3 by adding 5 M NH_3 (prepared from ammonia gas and deionized, distilled water) and transferred to a clean platinum crucible (25 ml) fitted with a Teflon coated magnetic stirrer. With the crucible as cathode and with a platinum foil anode the copper ions removed by electrolyzing at 0.5 amperes for 6 hours. The pH of the solution was adjusted to 6-8 with 0.5 M NH_3, after which it was poured through a small column (0.8 cm diameter, 2 cm long) of Chelex-100 ion exchange resin * (Bio-Rad Laboratories) in the ammonium form. At pH $\geq$ 5, this resin quantitatively retains cupric ion even from concentrated ammonium salt solutions (166,167). The resulting ammonium

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* The gift of a sample of the resin from the Noranda Research Centre is gratefully acknowledge.

TABLE 29

ABSORBANCE OF 5 x 10^{-5} M CHLORANILIC ACID AT 332 nm AS A FUNCTION OF SOLUTION pH AT 25°C

pH	A_{332}
0.84	0.13
1.65	0.24
2.94	0.69
3.01	0.73
3.29	0.89
4.33	1.19
6.52	1.25
8.30	1.25
9.18	1.26
9.63	1.25
10.69	1.25

FIGURE 45

DEPENDENCE ON pH OF THE ABSORBANCE AT 332 nm OF 5×10^{-5} M CHLORANILIC ACID

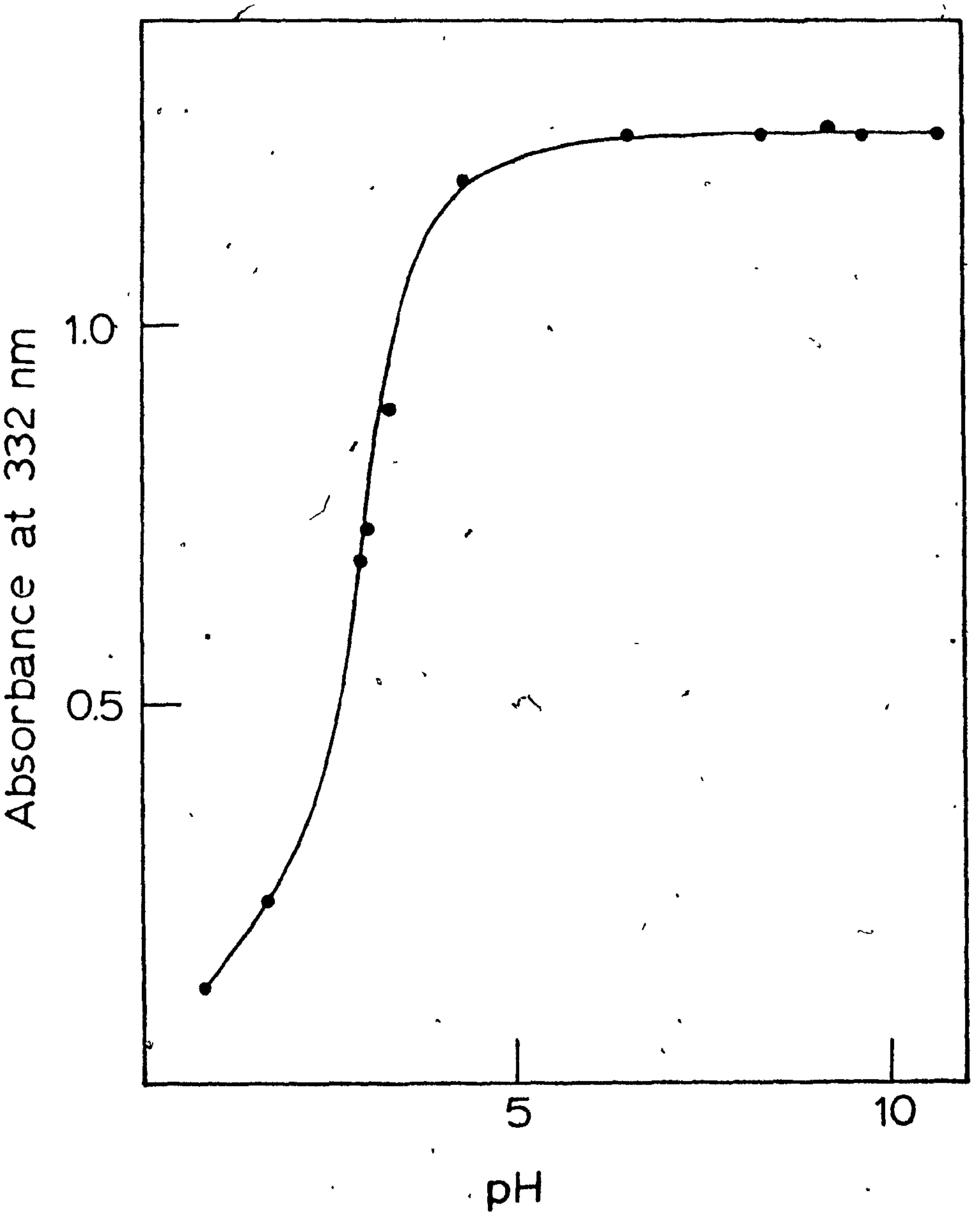

Absorbance at 332 nm
1.0
0.5
5
10
pH

TABLE 30

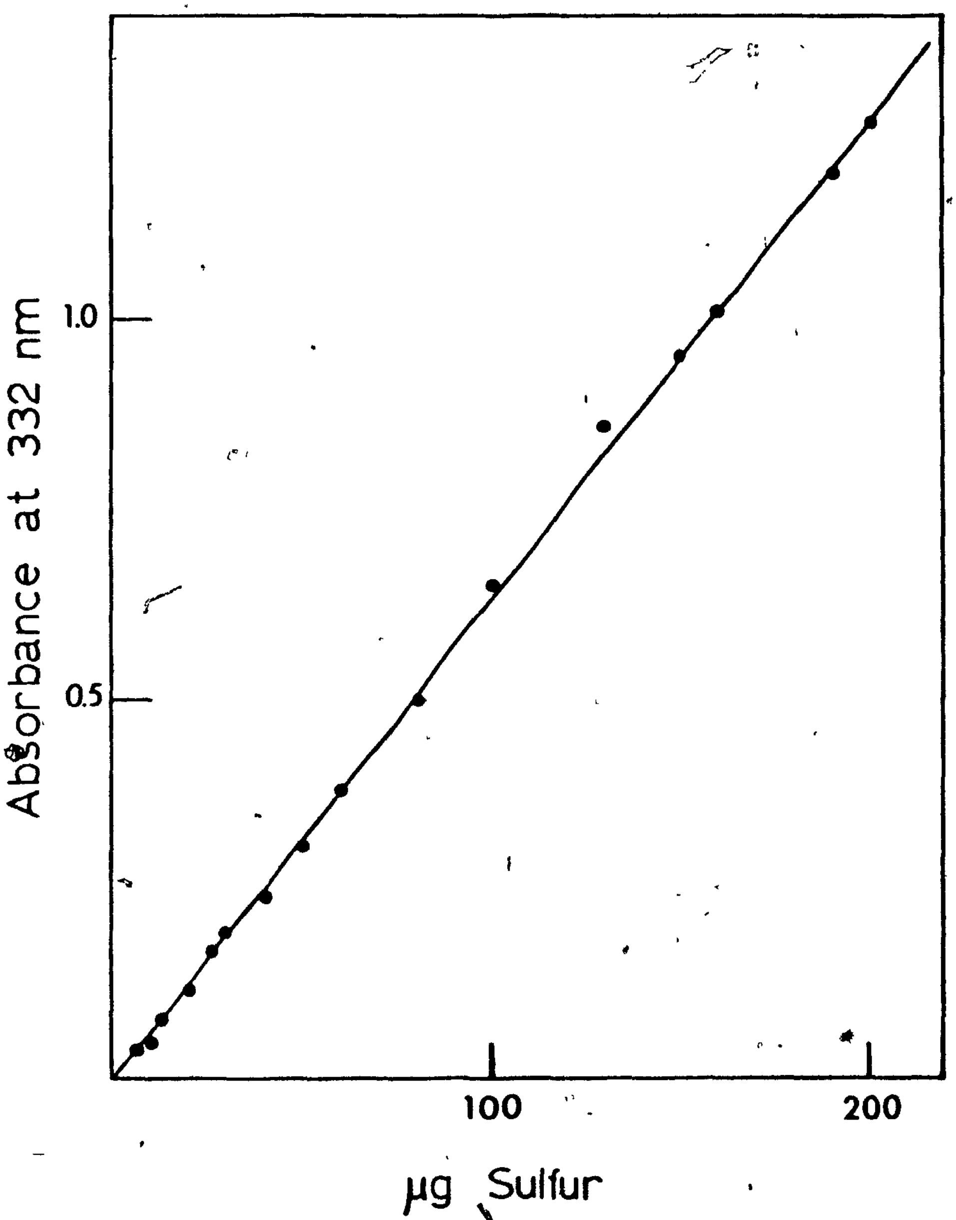
RELATION BETWEEN ABSORBANCE OF ACID CHLORANILATE ION AT 332 nm AND SULFATE CONTENT OF THE SAMPLE

μg S (as Na_2SO_4)	A_{332}
6.7	0.04
10	0.05
13	0.08
20	0.12
27	0.17
30	0.19
40	0.24
50	0.31
60	0.38
80	0.50
100	0.65
130	0.86
150	0.95
160	1.01
190	1.19
200	1.26
2000	1.26[a]
2000	1.25[a]

[a] – The last two absorbances were determined with 1 mm cells, all other values are for 10 mm path length.

FIGURE 46.

RELATION BETWEEN ABSORBANCE OF CHLORANILATE ION AT 332 nm AND THE AMOUNT OF SULFUR PRESENT IN THE FORM OF SODIUM SULFATE


Absorbance at 332 nm
1.0
0.5
100
200
µg Sulfur

nitrate solution ($\leq$ 38 ml) was contained in a 100 ml volumetric flask, to which were added 5.0 ml of 0.05 M potassium hydrogen phthalate and 50 ml 95% ethanol. The solution was made to volume with deionized water and 300 ± 20 mg of barium chloranilate added. The mixture was shaken mechanically for four hours and allowed to stand for a further 20 hours, to ensure complete reaction. Part of the solution was then centrifuged to remove suspended barium sulfate and chloranilate, and the absorbance at 332 nm determined using the Perkin-Elmer 402 UV-visible spectrophotometer. The absorbance of the blanks for copper deposited from standard electrolyte containing no thiourea was too high when a 10 mm cell was used, but with a 1 mm cell those preparations gave absorbance values of 0.44, 0.45 and 0.45 measured against a reference cell filled with water. The high absorbance was probably caused by the high nitrate concentration present as NH_4NO_3. The same effect was observed when chloride ion was present at high concentrations.

When sodium sulfate, equivalent to 1.00 mg sulfur was added to each of three solutions of copper deposited from the standard electrolyte, and the subsequent steps of the procedure followed as before, absorbances at 332 nm of 1.02, 1.06 and 1.08 (average = 1.05 ± 0.03) were measured in a 1 mm cell with water as a reference. Subtraction of the previous value of 0.45 ± 0.01 for the average absorbance of a solution of the deposit to which no sodium sulfate had been added yields an absorbance of 0.60 ± 0.04 due to the added sulfate. This is in good agreement with a value of 0.62 estimated from the calibration (Table 30) obtained in the absence of ammonium nitrate.

When three deposits obtained at 4.0 A/dm^2 in the presence of 10^{-3} M thiourea were treated by the procedure described above, absorbance values of 0.54, 0.51 and 0.49 at 332 nm were measured against a water reference. These values corresponded to 0.069, 0.045 and 0.030 weight per cent sulfur respectively (average, 0.048 ± 0.018 wt, %), for deposits obtained with the given conditions.

In several trial preparations of copper deposits to which the barium chloranilate estimation of sulfate was applied, it was noted that treatment of the deposit with dilute nitric acid (1M) at room temperature failed to remove a small amount of black residue that remained on the platinum. This could be dissolved only by adding more concentrated nitric acid, or by prolonged heating. In some cases, it was observed that mild heating with 1 N HNO_3 caused formation of small amounts (<< 1 mg) of a yellow hydrophobic substance which was assumed to be elemental sulfur. For a more thorough examination, two deposits of approximately 1.2 g each were obtained on the platinum cathode after approximately 22 hours at 0.8 A/dm^2 in standard electrolyte that had been made 0.01 M in thiourea. These deposits were dissolved in warm 1 N HNO_3 to yield several milligrams of an amorphous yellow substance. After drying at 105°C, this could be burned with a blue flame to give sulfur dioxide, it dissolved slowly in carbon disulfide, and it reacted slowly with cyanide solution to give thiocyanate (test with ferric ion). The yellow substance was thus identified as elemental sulfur. The black substance which was its precursor in the deposit proved to be copper sulfide, since a small amount of it heated with concentrated hydrochloric acid yielded hydrogen sulfide (detected by the deposition of black lead sulfide on a filter paper wetted with lead acetate solution).

A quantitative estimation was made of the amount of elemental sulfur produced by the warm nitric acid treatment of copper deposits obtained at 0.8 A/dm^2 from unstirred standard electrolyte containing 0.01 $\underline{M}$ thiourea. The elemental sulfur was separated by suction filtration, well washed with 2 $\underline{N}$ HCl followed by distilled water and dried in a vacuum desiccator for 24 hours. The sulfur was then transferred as quantitatively as possible to a small boat and weighed as sulfur, to yield values of 0.44 and 0.59 wt % sulfur in the deposits.

Cuprous sulfide, prepared by hydrolyzing pentathiourea dicuprous sulfate dihydrate in boiling 1 $\underline{N}$ NaOH, was found to yield over 90% of its theoretical sulfur content as elemental sulfur when treated with warm 1 $\underline{N}$ HNO_3. The remainder was presumably oxidized to sulfate (0.5061 g Cu_2S gave 0.0982 g S = 96%). Cuprous-thiourea complexes yielded neither elemental sulfur nor copper sulfide when treated with nitric acid.

To determine the extent to which sulfur might be present in the deposit in forms that did not yield elemental sulfur upon treatment with warm dilute nitric acid, deposits were prepared, as before, with thiourea concentrations of 0.01 M and 0.005 M. They were dissolved in 5.0 ml concentrated nitric acid and heated to drive off some of the excess acid. This procedure presumably oxidized all sulfur compounds present to sulfate, since there was no indication that elemental sulfur was liberated. The solutions were brought to pH ~ 3 with ammonium hydroxide and electrolyzed at 0.5 A in a platinum crucible that served as a cathode, with a platinum foil anode. When most of the copper had been removed, the solution was transferred to a small beaker and the nitrate removed by heating with several additions of concentrated hydrochloric acid. Barium chloride solution was added and the contents heated at approximately 80°C for 24 hours. The precipitate was then collected on Whatman No.42 ashless filter paper and ignited to constant weight. The deposit obtained in the presence of 0.01 M thiourea, at a current density of 0.8 A/dm^2, contained 0.65 wt % sulfur, a value in essential agreement with that obtained by determining elemental sulfur after dissolution of the deposit in warm

1 N HNO_3. When the thiourea concentration was 0.005 M, and the current density 0.8 A/dm^2, the sulfur content of the deposit was found to be 0.39 wt %, while at 4.0 A/dm^2, and the same thiourea concentration it had decreased to 0.24 wt %.

ELECTRON MICROPROBE ANALYSIS OF SULFUR IN COPPER ELECTRODEPOSITED FROM STANDARD ELECTROLYTE CONTAINING THIOUREA

A relatively thick deposit (~ 0.01 cm) of copper was prepared at 4.0 A/dm^2 from standard electrolyte containing 10^{-3} M thiourea. The deposit was cross-sectioned, embedded in plastic and polished. The sulfur in the cross-sectional area was measured* in an Acton (Camech) MS-64 electron microprobe analyzer by bombarding the surface with high energy electrons and measuring the sulfur K_α x-rays emitted from the sample. Cuprous sulfide (20.155 wt % S = 16872 + 171 counts per 10 sec.) and relatively sulfur-free copper foil (172 ± 8 counts per 10 sec) were used as standards from which the sulfur content of the deposit could be estimated. The background sulfur level in the copper foil substrate (Fisher) was 0.021 ± 0.001 wt % S, and the average value over a 200 μ x 200 μ area of the electrodeposit cross-section was

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* The author is grateful to Mr. Mark Firth, Department of Metallurgical Engineering, for determing these values.

0.044 ± 0.001 wt % S. The local sulfur content (for areas ~ 3μ in diameter) was found to decrease with time of deposition from an initial value of 0.055 ± 0.004 wt % S to a final value less than 0.033 ± 0.002 wt % S.

The sulfur was apparently not randomly distributed in the deposit. Some small areas contained very high concentrations of sulfur (≳ 1%, see Figure 47) while others appeared to be almost free from occluded sulfur. This method gives no information about the form in which the sulfur is present, but it may be assumed from the results presented earlier, that it is predominantly in the form of copper sulfide occlusions.

A summary of the data obtained for sulfur contents of deposits produced with different conditions of electrolysis with the different methods of estimation used, is presented in Table 31. From these data, it is possible to estimate surface coverage by addition agent corresponding to the sulfur contents found, and the calculated average surface coverages during deposition are shown in the last column of Table 31.

SOURCE OF THE SULFIDE OCCLUSIONS FOUND IN COPPER DEPOSITED FROM STANDARD ELECTROLYTE CONTAINING THIOUREA

The sulfur occluded in copper deposits obtained from standard electrolyte containing thiourea apparently was present almost exclusively in the form of copper sulfide (probably non-stoichiometric). It was of interest, therefore,

TABLE 31

SULFUR CONTENT OF COPPER ELECTRODEPOSITED FROM STANDARD ELECTROLYTE CONTAINING THIOUREA

[Tu] <u>M</u>	i A/dm^2	wt deposit g	% S	θ_{av}
0.010	0.8	1.1992	0.65[a]	0.034
0.010	0.8	1.1659	0.44[b]	0.023
0.010	0.8	1.4210	0.59[b]	0.031
0.005	0.8	1.1007	0.39[a]	0.020
0.005	4.0	1.4937	0.24[a]	0.012
0.001	4.0	0.2041	0.069[c]	0.0036
0.001	4.0	0.1994	0.045[c]	0.0023
0.001	4.0	0.2019	0.030[c]	0.0016
0.001	4.0	-	0.044[d]	0.0023

a - determined as barium sulfate
b - determined as elemental sulfur
c - determined with barium chloranilate
d - determined by electron microprobe analysis

FIGURE 47

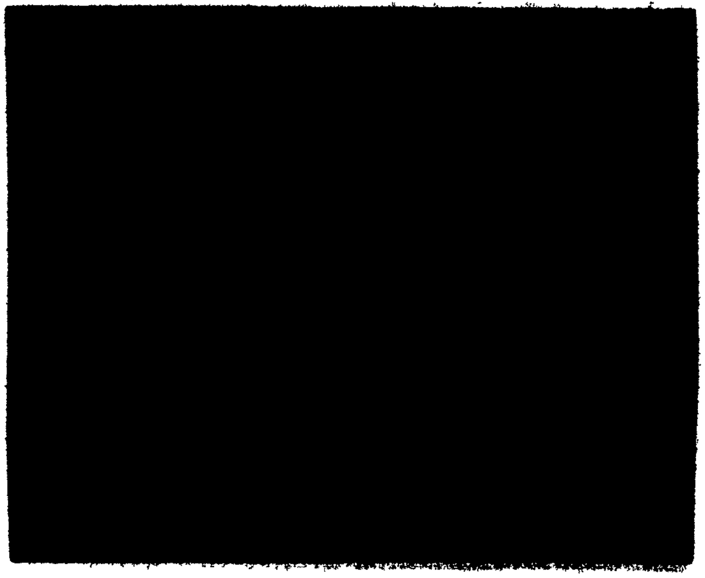
ELECTRON MICROPROBE ANALYSIS OF THE CROSS-SECTION OF COPPER DEPOSITED AT 4 A/dm^2 FROM STANDARD ELECTROLYTE CONTAINING 10^{-3} M THIOUREA. LIGHT AREAS INDICATE THE PRESENCE OF SULFUR.

TOP PHOTOGRAPH

THE HIGH SULFUR CONTENT REGION COINCIDED WITH A VISIBLE FAULT CONTAINING A BLACK SUBSTANCE THAT WAS PRESUMABLY COPPER SULFIDE.

BOTTOM PHOTOGRAPH

THE DIFFERENCE IN SULFUR CONTENT BETWEEN THE DEPOSIT COPPER AND THE SUBSTRATE IS SHOWN AS A HORIZONTAL LINE NEAR THE CENTER.



to determine how the thiourea or its reaction products were degraded to sulfide during deposition.

Using the two compartment electrolysis vessel described earlier, a solution containing 0.100 M thiourea in 0.05 M H_2SO_4 was electrolyzed with a copper foil cathode and platinum anode. The passage of currents greater than 20 $\mu A/cm^2$ was accompanied by slow but visible gas evolution which became more vigorous when the current was increased to 10 mA/cm^2 (electrode potential - 800 mV vs SCE). Hydrogen sulfide could not be detected with the lead acetate paper test, and the gas was presumably hydrogen. No changes were visible on the electrode, as long as it was cathodic, but after an hour on open circuit crystals of complex could be seen on the copper.

When a copper foil was made anodic in the acid thiourea solution, formation of needles of cuprous-thiourea complex both on the copper and in the solution became evident. If a copper foil were made to serve briefly as an anode in acid thiourea solution, and then made cathodic, its surface turned black immediately. Hydrogen sulfide was evolved when the blackened copper was treated with concentrated hydrochloric acid (lead acetate test).

When a clean copper foil was made a cathode in an acid thiourea solution containing pentathioureadicuprous sulfate dihydrate, it became black immediately with a film of copper sulfide. A platinum cathode also blackened in an acid solution of the same cuprous complex. When a copper foil was made an anode at a current density of 1 A/dm^2 in a fresh solution of 0.05 M formamidinedisulfide sulfate monohydrate in 1 M sulfuric acid, the blue color of cupric sulfate appeared in the vicinity of the anode, and no visible formation of sulfide occurred when the current was reversed.

From these observations, it would seem that cuprous-thiourea and possibly cupric-thiourea complex ions are cathodically reduced to sulfide at platinum and copper, whereas formamidinedisulfide is reduced to thiourea only at very negative potentials.

Steady state polarization data could not be obtained for the cathodic reduction of cuprous-thiourea complexes. Even at low current densities, continually increasing coverage of the electrode by sulfide caused an increase in electrode potential to a steady value of approximately -800 mV (vs SCE), at which obvious hydrogen evolution occurred.

DETERMINATION OF THIOUREA IN ACID COPPER SULFATE SOLUTIONS

The problem of determining the amount of "active thiourea" in acid copper sulfate solutions remains to be discussed. Since formamidinedisulfide as an oxidation product of thiourea does not appear to act as either a brightener or leveller, it would seem that the required analytical method should respond to thiourea and its complexes with cupric and cuprous ions. The measurement of UV absorbance in the region about 340 nm could be used, provided the absorbances due to cupric and cuprous-thiourea complexes could be resolved. A direct potentiometric determination using the potential of the formamidinedisulfide-thiourea couple is not possible (168) but measurement of the oxidation current of thiourea with a rotating platinum electrode has been used. (169)

In the present investigation the total concentration of thiourea and its complexes was determined by potentiometric titration with ceric ion, which does not affect formamidinedisulfide in strong acid. The method should estimate all species in solution that may be oxidized with ceric ion, i.e., cuprous ions and thiourea, but the concentration of each species cannot be so estimated. Moreover, cuprous ions formed in the oxidation of thiourea by cupric ions were stabilized by complex formation with unreacted thiourea, with the result that the total concentration of substances oxidized by ceric ion was essentially constant.

When filtered, finely dispersed air was rapidly bubbled through solutions that initially contained 0.025 M thiourea and 0.025 M cupric sulfate in 1 M sulfuric acid, and aliquots were titrated with ceric ion at various times, it was found that more than one-half the initial concentration of oxidizable substances remained in solution even after 5½ hours (Table 32), in spite of the fact that significant amounts of solid cuprous-thiourea complex had formed. It may be concluded from this that cuprous-thiourea complexes in aqueous solution are not rapidly oxidized by atmospheric oxygen. This would indicate that a bath containing thiourea in acid copper sulfate should become relatively stable after part of the thiourea has been oxidized and the remainder complexed with cuprous ions formed during the oxidation reaction.

DISCUSSION

The current efficiency data for deposition from acid copper sulfate containing 10^{-3} M thiourea indicate only a small amount of thiourea occluded in the deposit, and a negligible "deposit excess weight" under these conditions. This is confirmed by the quantitative analyses for sulfur occluded in the deposit.

The polarization measured in the presence of thiourea is high. The data show no easily discernible trend, except that the overpotential is less, the smaller the thiourea concentration. The high polarization may be ascribed to several contributory factors, and most of these can be assessed only in a qualitative manner.

TABLE 32

DETERMINATION OF SUBSTANCES OXIDIZED BY CERIC ION IN SOLUTION OF THIOUREA IN ACID COPPER SULFATE AT 25°C.

Time after mixing (min)	Concentration of oxidizable substances (N)
0	0.0245
3	0.0238
18	0.0235
34	0.0207
50	0.0201
87	0.0175
117	0.0164
158	0.0154
252	0.0139
336	0.0128

Gauvin and Winkler (170-172) have demonstrated that the measured polarization during copper deposition from pure electrolyte depends on the true surface area of the electrode. Obviously, a levelling agent such as thiourea must decrease the true surface area of the electrode as it exercises its levelling effect. Since roughness factors of 1.9 ± 0.2 (173) have been determined for electropolished copper, it is obvious that changes in true surface area due to levelling of a surface with a much larger roughness factor can cause a large increase in the true current density. This effect is impossible to assess quantitatively under electroplating conditions, but gas adsorption methods might be used to obtain information for the final surfaces.

The extent to which the levelled surface may be blocked by occluded sulfide can be roughly estimated from the sulfur content of the deposit. Assuming completely random distribution of sulfide ions through the crystal lattice, it may be estimated that the maximum possible average coverage by sulfur is of the order 10 to 20% of the surface area. Since sulfur, but little carbon, from the thiourea molecule is occluded in the deposit, the other fragment of the thiourea molecule, probably cyanamide, must tend to accumulate in the diffusion layer. Adsorption of part of this cyanamide onto the copper would further decrease the electrode area available for current flow, as would also any adsorption of formamidinedisulfide and complexes of thiourea. Finally, the presence in the diffusion layer of a multitude of crystal nuclei (each containing perhaps only 20-100 molecules of insoluble cuprous-thiourea complex) may so increase its viscosity, and otherwise hinder transmission of ions through it, that the overpotential is appreciably increased. If several factors such as these can affect the ease of deposition, it is not surprising that the overpotential values are high, and, at least with high concentrations of thiourea ($> 10^{-3}$ M), are not strongly correlated with thiourea concentration and apparent (geometric) current density. The decrease in true surface area due to levelling and the irreversible formation of sulfide are factors that preclude the application of the simple site-blocking theory to interpret the overpotential increase caused by thiourea.

The sulfur determinations indicate that sulfide is the predominant form in which the sulfur from thiourea is occluded in the deposits. The photomicrograph of a crystal of complex on the surface of the deposit (Figure 37) proves that relatively large crystals of complex may also be occluded, but the analyses show that this contribution is relatively small. While electron microprobe analyses apparently show the distribution of sulfur in the deposit to be non-random, the resolution of approximately 3 x 10^4 Å does not allow the size of the individual sulfur occlusions to be determined.

Steinemann and Hintermann (154) used transmission electron microscopy to investigate occlusions in copper electrodeposited from an acid copper sulfate solution containing thiourea (5 mg/l) and pyridine (20 mg/l). They made one deposit at 2 A/dm^2, which they found to contain approximately 1.9 x 10^{17} occlusions per cubic centimeter, with an average occlusion diameter of 25 Å (resolution, 6 to 7 Å). For the given conditions of deposition, the total volume of occluded material constituted approximately 0.3% of the total volume of the deposit. The chemical nature of the occlusions was not determined, but if it is assumed that the occlusions were entirely sulfide ion (i.e. negligible pyridine), with a diameter of approximately 3.7 Å, it may be estimated that the deposit should contain 0.01 to 0.04 wt % S. This sulfur content is in good agreement with values that would be expected on the basis of sulfur contents determined in the present study. Moreover, the average diameter, 25 Å , of the occlusions would correspond to the order of 100 to 300 sulfide ions in each occlusion. Such aggregates might well correspond to the occlusion of relatively large aggregates of complex that presumably form in the solution, or in the diffusion layer, as crystal nuclei. These nuclei could be adsorbed onto the cathode surface and, because of the copper-sulfur bridging bonds in the "polymeric" complex, suffer reduction to sulfide by charge transfer through these bonds. The potential required for this reduction would probably increase with increased size of the adsorbed nuclei. With sufficiently large agglomerates, electroreduction might fail to occur, and the larger crystals retain their identity in the deposit, as observed (Figure 37). The potential required for reduction of the complex could not be determined with the galvanostatic method used in this investigation, but it could be found by measuring the ratio of carbon to sulfur occluded under potentiostatic conditions. The electrode potential at which the carbon-to-sulfur atom ratio deviated from unity would represent the minimum average electrode potential required for electroreduction of cupric or cuprous-thiourea complexes. However, from the data on electrode polarization, and sulfur occlusion in deposits obtained from solutions containing thiourea, reduction of the complex must have occurred in the potential range from + 300 to approximately 0 mV (vs SHE) under the present conditions.

Reduction should occur, presumably, at any localized area on the electrode where the required minimum potential for reduction is attained. If this be true, a tentative explanation may be offered for the levelling effect of thiourea in copper electrodeposition.

In practice, a real electrode surface must represent a rough surface with various protrusions and outside edges. The local electric field strength in these areas should be higher than on level parts of the electrode or in recesses and cavities. In the absence of thiourea, these areas of high field strength would be expected to carry a higher current density and to grow a deposit more rapidly than the areas of lower electric field strength. In the presence of thiourea, the opposite is found to occur (51) and only small amounts of copper with a high concentration of occluded sulfur are deposited on the peaks. Several workers have attributed this apparent reversal to variations in thickness of the diffusion layer over protrusions and recessed parts of the electrode surface (c.f. General introduction, diffusion theory, p. 12, also ref. (48)). However, an alternative explanation of the levelling effect is possible if it is assumed that adsorption onto the electrode of cuprous-thiourea complex (in the form of molecules and/or of crystal nuclei) possesses a degree of reversibility at potentials lower than that required for reduction to sulfide, while reduction to sulfide in areas of high field strength (i.e. on the peaks) leads to irreversible blockage of these areas. Deposition would then occur around these sulfide occlusions, preferentially in the areas of lower field strength where reduction to sulfide does not occur as readily. With progress of the levelling process, selective reduction and inhibition to deposition should decrease, and continuity of the levelled surface become more prevalent.

The decrease in levelling power when solutions of thiourea in acid copper sulfate are aged cannot be explained by complete conversion of thiourea to the disulfide, since a large fraction of the thiourea is converted to cuprous-thiourea complexes, which protect the coordinated thiourea from oxidation by cupric ion. The cuprous-thiourea complex is also too stable to attribute the change to its oxidation by atmospheric oxygen. The decreased amount of sulfur occluded with aged solutions might be interpreted to indicate that the cupric-thiourea complex initially formed is the only surface-active species. However, this would seem to be contrary to the observation that plating baths retain their levelling powers even after sufficient time has passed to allow complete conversion of the cupric complex to cuprous complexes and formamidinedisulfide.

It is possible that the change in levelling power with ageing has its origin in the aggregation of cuprous-thiourea complex to form crystal nuclei and eventually microscopic and macroscopic crystals. These polymolecular species, like their monomeric progenitors, might have the beneficial properties of an addition agent, but it is reasonable to expect that their effectiveness should decrease with increase in size. For example, four nuclei each containing one hundred complex units might reasonably be expected to be more effective in levelling than one larger nucleus containing 400 complex units. The levelling powers of thiourea in copper sulfate electrolyte should therefore decrease as the cuprous-thiourea complexes contribute to continued growth of crystal nuclei during the ageing process. At very low thiourea concentrations ($\geq$ 10^{-3} *M*), it requires two or more weeks for crystals to become visible to the naked eye. During this time, however, polymolecular nuclei of complex must obviously be present in the solution. In a commercial system that is electrolyzed continuously (e.g. copper electro-refining), the occlusion of various species during deposition would probably be too rapid to permit formation of visible crystals of complex. Nevertheless, a progressive deterioration of the levelling effects of bright copper baths that contain higher thiourea concentrations might be ascribed to the gradual disappearance of molecular complexes to form less effective polymolecular aggregates, without the appearance of macroscopic crystals.

GENERAL REMARKS

GENERAL REMARKS

In contrast to the present investigation, no previous study of addition agents appears to have given prior consideration in any detail to the possible chemical interactions between the additive and the electrolyte in the absence of electrodeposition. Failure of previous workers to examine the thermodynamic and kinetic characteristics of such reactions between thiourea and the electrolyte, and to establish definitely the identity of various species produced, probably accounts for the conflicting experimental data that have been published.

As one example of the advantages gained by the type of approach made in the present study may be cited the observation that much of the thiourea is oxidized to formamidinedisulfide, which possesses appreciable stability at the high acid concentrations and relatively low temperatures used, but apparently does not contribute significantly as a levelling agent. The significance of its formation and continued presence in the system must therefore be evaluated in this context.

As another example, it may be recalled that the thiourea complex with the UV absorption band at 340 nm was revealed by detailed study to be a cupric complex rather than a cuprous complex, as suggested by Javet and Hintermann.

The mistaken identity attributed to it by these investigators made them unable to explain the observation that the absorbance of the band at 340 nm decreased more rapidly in the anode compartment than in the cathode compartment of their cell during electrolysis (156). Since the cathodic consumption of thiourea had been shown to be diffusion controlled under these conditions (151), it was obvious that the anodic consumption of thiourea could not be faster if it,too, relied on diffusion of the same species. However, the decrease with time of the band intensity is due not only to "consumption" of thiourea at the electrodes, but also to the conversion of the cupric-thiourea ion to the cuprous complex with a lower molar absorptivity in the region of the absorption maximum. The reaction of thiourea with anodically generated cuprous ions corresponds, therefore, to a more rapid apparent consumption (measured by UV) anodically than cathodically and the seeming contradiction is explained.

Even more detailed information about the reactions and equilibria involving thiourea and the electrolyte, and about the formation and incorporation of sulfide during electrodeposition, will probably be required for more complete elucidation of the addition agent behaviour of thiourea. Attempts to clarify the relation between the physico-chemical and electrochemical aspects of the system would seem to have considerable advantage over the more conventional approach in which electrochemical and physical data, such as polarization, reflectance, double layer capacitance, etc., are emphasized, with little attention to their dependence on the chemical reactions that may underlie the electrochemical behaviour.

Perhaps the most interesting conclusion to emerge from the chemical and electrochemical studies that have been presented is that the levelling and brightening effects of thiourea as an addition agent are to be attributed to the monomolecular complexes of thiourea with cupric and cuprous ions, and the polymolecular cuprous-thiourea complexes. The uncomplexed thiourea molecule appears to contribute little or nothing to the beneficial effects that accrue from its presence in the electrolyte. It is interesting to note that the sequence of reactions proposed to explain levelling and brightening by thiourea necessitates the occlusion of appreciable quantities of sulfide in the deposit. It would appear likely that a certain range of sulfur contents of the deposits will give smooth and bright copper deposits. Too much or too little sulfur seemingly is deleterious to the process.

The sulfur-copper ratio in the deposit is governed by the applied current density, which controls the rate at which copper is deposited, and by the rate at which complexes of thiourea arrive at the cathode. At a sufficiently high cathode overpotential, all complex arriving at the cathode will be reduced to sulfide and the cathodic consumption of thiourea will be diffusion controlled. Therefore, the proper (optimum) flux of copper-thiourea complexes at the cathode may be maintained by adjusting either the bulk thiourea concentration in an unstirred solution, or by stirring the electrolyte and lowering the thiourea concentration correspondingly.

In view of the specific sulfur-copper ratio apparently required for a bright deposit, it may be argued that copper sulfide is specifically responsible for modifying the deposit. The complexes of thiourea can then be regarded simply as a source from which copper sulfide is generated in those areas where it is required for levelling to occur, e.g., at micro-peaks on the surface.

For a more complete description of the system, it would seem desirable to determine to what extent the sulfide is generated from the monomeric complex ions $[CuTu]^{2+}$ and $[CuTu]^{+}$ rather than from polymolecular aggregates of cuprous-thiourea complex. At the present time, however, there is no method available for studying copper deposits with a resolution sufficient to determine single atoms of sulfide in a copper lattice. A method such as transmission electron microscopy might enable estimation of the amount of sulfur contained in the larger occlusions in the deposit. This, in conjunction with a value for the total sulfur content of the deposit (electron microprobe analysis) should then give, indirectly, an indication of the amount of sulfur occluded in the deposit in the form of single molecules of copper sulfide.

Some other points that merit further study are the adsorption-desorption of thiourea (in the form of its cuprous complexes) at copper surfaces and, study of ~~the~~ growth of polymolecular assemblies of cuprous-thiourea complex in the electrolyte. As mentioned previously, the data that supposedly refer to adsorption of thiourea at copper were obtained under experimental conditions that favoured hydrolysis of cuprous-thiourea complexes to copper sulfide. It is doubtful, therefore, that they represent true adsorption of thiourea. As a consequence, there are no quantitative or even qualitative results available that might give information about the strength of the adsorption bond, or the ease with which adsorbed complexes might desorb from the copper.

A study of the growth of polymolecular aggregates of cuprous thiourea complex might yield data on the size of these particles at various times after addition of thiourea to the electrolyte. These values might then be correlated with the levelling power of the bath and the amounts of sulfur and carbon occluded in the deposits obtained from these systems. In this way, the relative addition agent powers of the particles with increasing size might be assessed, to enable optimum levelling and brightening to be established and maintained in solutions of acid copper sulfate that use thiourea as addition agent.

SUMMARY

AND

CONTRIBUTIONS TO KNOWLEDGE

SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

1) Formamidinedisulfide sulfate has been shown to exist as the monohydrate, rather than the anhydrous salt claimed by previous workers.

2) In acid solution, the hydrolysis of formamidinedisulfide approximated the classical Schiller-Otto stoichiometry, with 1.5 moles of thiourea produced for each mole of disulfide that was hydrolyzed.

3) The rate of the hydrolysis in acid solution was determined from the initial rate of change of absorbance of the disulfide solution at the wavelength of maximum absorbance for thiourea. This method was applied to both formamidinedisulfide and di-(tetramethylformamidine)disulfide in hydrochloric acid solution and the hydrolysis reactions were found to obey the rate expression

$$\text{Rate} = k\,[\text{disulfide}][\text{hydroxide}]$$

The activation energy and entropy of activation over the range 20 to 40°C for the hydrolysis of formamidinedisulfide at pH < 4 were found to be 7.8 kcal mole^{-1} and -2 e.u. respectively. The corresponding values for di-(tetramethylformamidine)disulfide were 1.8 kcal mole^{-1} and 16 e.u..

The stoichiometric and kinetic data were in agreement with nucleophilic attack by hydroxide ion at the disulfide bond, with cleavage of the -S-S- bond in the transition complex constituting the rate-determining step.

4. At pH > 5, the hydrolysis of formamidinedisulfide was too rapid for kinetic study, but the stoichiometry was in agreement with a mechanism that involved deprotonation of the amidinium group by hydroxide ion as the first step. This mode of hydrolysis led to the immediate formation of elemental sulfur.

5. Trithioureadicuprous sulfate monohydrate has been isolated as a new, insoluble complex in the reaction of thiourea with a large excess solution of 0.5 M cupric sulfate in 1.0 M sulfuric acid. A band at 250 cm^{-1} in the Raman spectrum of the compound has been tentatively assigned to a copper-sulfur stretching mode.

6. The UV absorption maximum found at 340 nm when thiourea is added to acid copper sulfate solution has been assigned to a cupric-thiourea ion with a molar absorptivity of approximately 3300 M^{-1} cm^{-1} and a stability constant at 25°C of 2.2 ± 0.2 in solutions of cupric sulfate and sulfuric acid. The absorption is due to a charge transfer from sulfur to cupric ion in the

sulfur-bonded complex. The value of the absorbance at times other than t ~ 0 is a superposition of the charge transfer band and absorbance due to cuprous-thiourea complex.

7. Dark red needles of di-(tetramethylthiourea) cupric chloride have been prepared in high yield from solutions in isopropanol. Broad absorption bands of the solution of the complex in the region of 410 and 520 nm are apparently caused by at least two different species involving cupric chloride and tetramethylthiourea.

8. In dilute aqueous solution tetramethylthiourea is rapidly and completely oxidized by cupric ion to di-(tetramethylformamidine)disulfide.

9. The colorimetric determination of sulfate ion with barium chloranilate has been adapted to the estimation of sulfur compounds occluded in electrodeposited copper at a level of approximately 0.05 wt % sulfur.

10. Previous workers have demonstrated cleavage of the thiourea molecule during electrodeposition (using radiotracers), and the sulfur was assumed to be present in the form of sulfide. No chemical proof was given, however, to support this claim. In this investigation it has been shown that at thiourea concentra-

tions above 10^{-3} M in the electrolyte the occluded sulfur is present in the deposit almost exclusively in the form of sulfide.

11. Cuprous-thiourea complexes in aqueous solution are electrochemically reduced to copper sulfide at cathodes of copper or platinum.

12. Formamidinedisulfide appears to have little effect upon electrodeposition from acid copper sulfate solution at current densities less than approximately 4 A/dm^2.

13. The uncomplexed thiourea molecule has little or no effect on the deposition process.

14. Copper sulfide formed by reduction of cuprous and cupric complexes of thiourea was responsible for changes in the structure of copper electrodeposited from acid copper sulfate solutions to which thiourea had been added. Levelling and brightening may be explained by preferred reduction of complexes of thiourea at peaks on the electrode.

15. The decrease in the levelling powers of the bath with time after addition of thiourea appeared to be caused by agglomeration of monomolecular complexes of thiourea with cuprous ions to form polymolecular aggregates of insoluble complexes of thiourea with

cuprous sulfate.

16. The site blocking theory is not applicable to explain quantitatively the high overpotentials measured for copper deposition from electrolyte containing thiourea.

17. With thiourea as addition agent for acid copper sulfate baths, levelling and brightening of the deposit are not possible without the occlusion of appreciable quantities of sulfide ($\gtrsim$ 0.01 wt % sulfur).

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