$(CH_3)(CO)_2P(OCH_3)_3$, 68170-31-0; η^5-$C_5H_5Cr(H)(CO)_2P(OCH_3)_3$, 68122-41-8; η^5-$C_5H_5Cr(H)(CO)[P(OCH_3)_3]_2$, 60541-12-0; cis-$\eta^5$-$C_5H_5Cr(COCH_3)(CO)_2P(OCH_3)_3$, 68170-28-5; trans-$\eta^5$-$C_5H_5Cr$-$(COCH_3)(CO)_2P(OCH_3)_3$, 68170-29-6.

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(14) Cp denotes the center of gravity for the five-membered ring of the cyclopentadienyl ligand.
(15) A complete description of the experimental conditions and structure refinement for $[\eta^5$-$C_5H_5Cr(CO)_2P(OCH_3)_3]_2$, **2**, and η^5-C_5H_5Cr-$(CO)_2[PO(OCH_3)_2]P(OCH_3)_3$, **3**, will be published in a separate paper along with detailed comparisons of the resulting parameters with those of related molecules.
(16) See J. W. Faller and A. S. Anderson, *J. Am. Chem. Soc.*, **92**, 5852 (1970), for discussion of $C_5H_5ML_4$ complexes and of dynamic conformational features of these complexes.
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Oxidation of Thiourea and N,N'-Dialkylthioureas by Hexachloroiridate(IV) Ion

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The kinetics of the oxidation of thiourea (TU), N,N'-dimethylthiourea (DT), and 2-imidazolidinethione (IT) by $IrCl_6^{2-}$ in aqueous perchlorate solutions followed a third-order rate law, second order with respect to thiol concentration and first order with respect to $IrCl_6^{2-}$. The third-order rate constants were obtained from the slopes of k_{obsd} vs. [thiol]^2 plots under the following reaction conditions: $[IrCl_6^{2-}] = 2.00 \times 10^{-4}$ M, [thiol] $= 1.00 \times 10^{-3}$ to 0.015 M, pH 1.10, $\mu = 0.15$ M, and 25.0 °C. The values of k_3 obtained are 368, 394, and 297 M^{-2} s^{-1}, respectively, for TU, DT, and IT. When pH is varied from 1.10 to 4.67, a pH–rate profile is observed with constant rate at pH range 1.10–2.3 and a rapid increase in rate as the pH is raised above 2.3. The activation parameters calculated from the temperature studies (20.0–35.0 °C) yielded $\Delta H^*_3 = 5.76$ (DT), 6.12 (TU), and 7.51 (IT) kcal mol^{-1} and $\Delta S^*_3 = -27.3$ (DT), −26.1 (TU), and −22.0 (IT) eu. A mechanism involving a fast preequilibrium step followed by disulfide radical formation is postulated to explain the kinetic behavior.

Introduction

The kinetics and mechanisms of oxidation of thiourea and its N,N'-dialkyl derivatives by different aquo complexes of metal ions[1] such as Ce(IV), Co(III), V(V), Mn(III), OsO_4, and Cu(II) and the EDTA and HEDTA complexes of Cu(II)[2] have been reported. In V(V), OsO_4, and Cu(II) oxidations, thiourea complexes of the metal ions have been reported. The electron-transfer mechanism that has been postulated for the metal aquo ions oxidations appeared to be inner sphere. The usual kinetics of these reactions is second order overall with an inverse dependence in [H$^+$] term. Only the EDTA and HEDTA complexes of Cu(II) show second-order dependence in thiourea.

Recently, Hoffmann and Edwards[3] have reported the reaction mechanism for the oxidation of thiourea and its N,-N'-dialkyl derivatives by hydrogen peroxide. The mechanism they have postulated involves an activated complex of hydrogen peroxide and thiourea. This has been postulated to explain the large negative entropy of activation observed in these reactions.

In this paper we report the results of a study of the oxidation of thiourea (TU), N,N'-dimethylthiourea (DT), and 2-imidazolinethione (IT) ($E° = -0.42$ to -0.46 V[4]) to the corresponding disulfide compounds by the outer-sphere oxidant, $IrCl_6^{2-}$ ($E° = 1.02$ V).[5] This oxidant has been chosen

to circumvent the substitution rate-controlled reaction when metal aquo ions are used.

Experimental Section

Reagents. Thiourea (TU), N,N'-dimethylthiourea (DT), and 2-imidazolidinethione (IT) were obtained from Aldrich Chemical Co. Thiourea and 2-imidazolidinethione were extensively recrystallized from ethanol–water solution and DT was repeatedly recrystallized from dioxane solution until clear white crystals were obtained. All of the recrystallized compounds were dried under vacuum. The purities of the recrystallized compounds were checked by comparing the melting points and NMR and UV spectra with those from literature and Aldrich Spectra Handbook.

Sodium perchlorate solution was prepared by neutralizing anhydrous sodium carbonate with 70% perchloric acid. The concentration of sodium perchlorate was analyzed gravimetrically. The water used in the experiments was purified by passing through two ion-exchange columns and redistilled using an all-glass apparatus.

Potassium hexachloroiridate(IV) was obtained from Alfa Products (Ventron) and used without further purification.

Stoichiometry and Product Studies. The reaction stoichiometry for the oxidation of TU, DT, and IT was obtained using the following procedure. Excess $IrCl_6^{2-}$ was reacted with the reducing agents and the change in absorbance at 488 nm was used to determine the amount of $IrCl_6^{2-}$ consumed. In all three systems, a variable stoichiometry was obtained depending on the initial concentration ratios of $IrCl_6^{2-}$ and the reducing agents, Figure 1. The stoichiometry varies from 1 to approximately 6 depending on the initial concentration ratio of the reactants. At no time was an 8:1 stoichiometry observed as
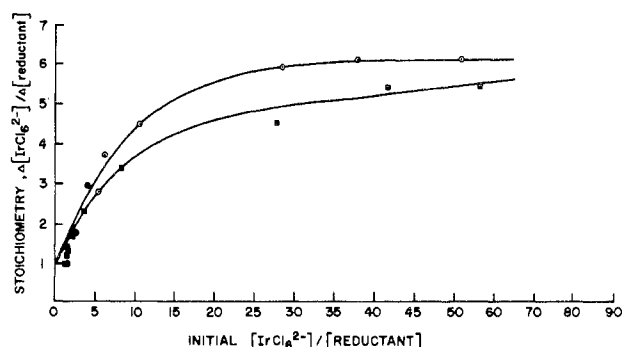
Figure 1. Variation of stoichiometry with initial $[IrCl_6{}^{2-}]$/[reductant]: opened circles, TU; opened squares, DT; filled circles, IT.

reported in the $Fe(CN)_6{}^{3-}$ oxidation of thiourea in basic solution.[6] The difference in stoichiometry could probably be due to the difference in acidity of the solutions where the reactions were carried out. This indicates that the initial products formed can be oxidized further by the excess $IrCl_6{}^{2-}$. However, stoichiometry ratios close to 1 are always obtained for all three cases when the concentrations of the reactants are about the same thus implying a 1:1 stoichiometry under the conditions employed for the kinetic studies, i.e., with excess reductant.

No product isolation and analysis were done for the variable stoichiometry studies. However, it should be noted that the maximum limiting stoichiometry of 6:1 is observed for the thiourea and $N,$-N'-dimethylthiourea oxidation. The higher stoichiometry does imply further oxidation of the disulfides by $IrCl_6{}^{2-}$.

Authentic samples of the appropriate disulfides were prepared by hydrogen peroxide oxidation. The strong UV absorption of the disulfides at around 230 nm was observed. Product solutions following oxidation by $IrCl_6{}^{2-}$ showed identical maxima in the UV.

The product of the oxidation of 2-imidazolidinethione by $IrCl_6{}^{2-}$ was isolated using a procedure similar to that described by Johnson and Edens.[7] Three hundred milligrams of K_2IrCl_6 and 0.60 g of IT in 100 mL of dilute HCl solution were reacted. It was warmed for 1 h with ethanol added. A yellowish brown powder was isolated after the solution was placed in the refrigerator for 12 h. The powder was filtered and washed repeatedly with distilled water to remove all the inorganic salt. Elemental analysis shows that the compound is $C_6H_{10}N_4S\cdot HCl$; mp 274 °C (lit. 280 °C).[7] Anal. Calcd: C, 34.87; H, 5.33; N, 27.12; S, 15.50; Cl, 17.19. Found: C, 34.93; H, 5.86; N, 26.66; S, 15.66; Cl, 16.89.

Duplicate carbon analysis was performed for accuracy. The probable structure of the hydrochloride salt conforming with the results of elemental analysis is shown.
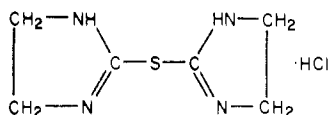
However, it is still rather inconclusive as to how this sulfide of IT was formed although it had been postulated that it probably was from the disulfide of IT.

Procedure. A Cary Model 14 recording spectrophotometer was used to record all the visible and UV spectra of the solutions as well as to monitor the kinetic studies. The cell compartment of the Cary 14 was thermostated at 25.0 ± 0.5 °C. Faster reactions were followed using an Aminco-Morrow stopped-flow spectrophotometer likewise thermostated at 25.0 ± 0.5 °C.

All the kinetic studies were conducted under pseudo-first-order conditions with the concentrations of the thiols in at least tenfold excess over $IrCl_6{}^{2-}$. The disappearance of $IrCl_6{}^{2-}$ was monitored at 488 nm, and the values of k_{obsd} were calculated from the slopes of log ($A_t - A_\infty$) vs. time plots. Fresh solutions at constant ionic strength and pH were prepared for each kinetic run to ensure reproducibility of the data. All kinetic measurements were done in replicate to obtain consistent results.

Results

The results from spectral studies under varied initial $[IrCl_6{}^{2-}]_0$/[reductant]$_0$ ratios suggest that a limiting 1:1 stoichiometry should exist under the kinetic conditions where

Table I. Oxidants Dependence

reacn conditions[a]	$10^4[IrCl_6{}^{-2}]$, M	$10^2 k_{obsd}$, s^{-1}
1. Thiourea		
[TU] = 1.00 × 10^{-2} M	1.66	4.61
pH 1.60	1.24	4.61
	0.82	4.56
	0.67	4.39
2. N,N'-Dimethylthiourea		
[DT] = 9.75 × 10^{-3} M	2.25	3.75
pH 1.10	1.08	3.75
	0.79	3.75
[DT] = 4.50 × 10^{-3} M	2.25	0.95[b]
pH 2.00	1.26	0.96
	0.52	0.96
3. 2-Imidazolidinethione		
[IT] = 1.00 × 10^{-2} M	2.45	3.16
pH 1.10	1.81	3.17
	0.93	3.32
[IT] = 4.50 × 10^{-3}	2.00	1.15[b]
pH 3.00	1.60	1.19
	1.00	1.18
	0.60	1.23

^{a} t = 25.0 °C and μ = 0.15 M. ^{b} See ref 8.

the reducing agent concentrations were always in large excess over $[IrCl_6{}^{2-}]$. A representative stoichiometric equation with TU is shown.

$$2IrCl_6{}^{2-} + 2(NH_2)_2CS \longrightarrow 2IrCl_6{}^{3-} + 2H^+ + \quad (1)$$
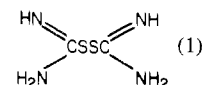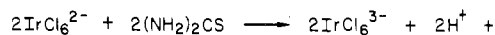
We have found that hydrogen ions were released in the reaction. This was accounted for by measuring the pH change in a reaction containing $[IrCl_6{}^{2-}] = 1.00 \times 10^{-3}$ M and [TU] $= 1.0 \times 10^{-2}$ M. Calculation based on the pH change showed that over 91% of the stoichiometric amount of hydrogen ions produced was accounted for. Several attempts to isolate the disulfides produced were not successful; however, the characteristic strong UV absorption at 230 nm strongly implies their presence in the reacted solutions.

Oxidant Dependence. In all the three systems studied, the kinetics were conducted under pseudo-first-order conditions where the reductant concentrations were in large excess over the $IrCl_6{}^{2-}$. The acid strength (pH 1.10 for DT and IT and 1.60 for TU) and the ionic strength (μ = 0.15 M) of the reacting solutions were adjusted with appropriate amounts of perchloric acid and sodium perchlorate solutions. The kinetics of the reactions were followed at 488 nm, the absorption maximum of $IrCl_6{}^{2-}$. Plots of log ($A_t - A_\infty$) vs. time were linear over at least 3 half-lives consistent with a first-order decrease in concentration of $IrCl_6{}^{2-}$, i.e.,

$$-d[IrCl_6{}^{2-}]/dt = k_{obsd}[IrCl_6{}^{2-}] \qquad (2)$$

As required by this rate expression, k_{obsd} stays unchanged when $[IrCl_6{}^{2-}]$ is varied at constant reductant concentrations (Table I).

The first-order dependence of $[IrCl_6{}^{2-}]$ was also examined at higher pH (2.0 for DT and 3.0 for IT) and constant thio concentration of 4.50×10^{-3} M with $[IrCl_6{}^{2-}]$ varied from 5.2 $\times 10^{-5}$ to 2.25×10^{-4} M. In each kinetic series of pH and fixed thio concentration the pseudo-first-order plots are linear with an average deviation from the mean k_{obsd} of 2.1%.

The effect of $IrCl_6{}^{3-}$ on the rate of reaction was also studied in one case. In the presence of 1.00×10^{-4} M $IrCl_6{}^{3-}$ which was generated in situ with $SO_3{}^{2-}$, reduction of half of the original $IrCl_6{}^{2-}$ did not change the values of k_{obsd} when
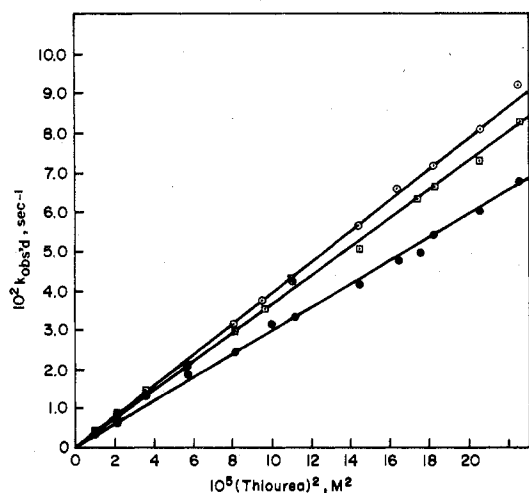
Figure 2. Plots showing the second-order dependence in thiourea concentration. Reaction conditions were 25.0 °C, $[IrCl_6^{2-}]$ = 2.00 × 10^{-4} M, pH 1.10, [thiol] = 3.00 × 10^{-3} to 1.50 × 10^{-2} M, and μ = 0.15 M: opened circles, DT; opened squares, TU; filled circles, IT.
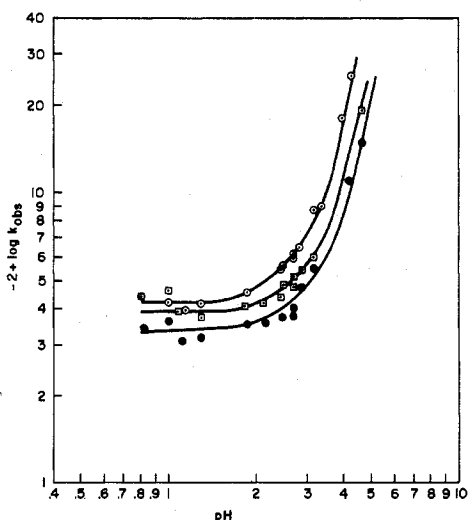
Figure 3. Rate–pH reaction profile. Reaction conditions were 25.0 °C, $[IrCl_6^{2-}]$ = 2.00 × 10^{-4} M, [thiol] = 1.00 × 10^{-2} M, and μ = 0.15 M: opened circles, DT; opened squares, TU; filled circles, IT.

compared to reaction with no $IrCl_6^{3-}$.

Dependence on Reducing Agent Concentrations. The dependence on reductant concentration was studied at 25 °C with $[IrCl_6^{2-}]$ = 2.00 × 10^{-4} M, μ = 0.15 M, and pH 1.10. The concentrations of the thioureas were varied from 3.00 × 10^{-3} to 1.50 × 10^{-2} M. The rate dependence with respect to thiourea concentration is second order as shown by the linear plots of k_{obsd} vs. [reductant]^2 in Figure 2. The observed rate law for the three systems can therefore be expressed as

$$-d[IrCl_6^{2-}]/dt = k_3[IrCl_6^{2-}][thiourea]^2 \qquad (3)$$

The values of k_3 evaluated from the slopes of the linear plots in Figure 2 for the oxidations of thiourea, N,N'-dimethylthiourea, and 2-imidazolidinethione (ethylenethiourea) are 368, 394, and 297 M^{-2} s^{-1}, respectively.[8]

pH Dependence. The effect of pH on the rate of reaction was studied at 25 °C with $[IrCl_6^{2-}]$ = 2.00 × 10^{-4} M, [thiourea] = 1.00 × 10^{-2} M, and μ = 0.15 M. The pH of the reacting solution was adjusted with an appropriate amount of perchloric acid. The rates of oxidation of all three thioureas appear to be unchanged at low pH (0.8–2.3). However, a rapid increase in rate is observed when the pH of the solution is

Table II. Copper Catalysis[a]

[Cu(II)] added	$10^2 k_{obsd}$, s^{-1}		
	TU	DT	IT
none	2.90	4.05	3.30
2.4 × 10^{-6} M	4.06	8.60	3.60
6.0 × 10^{-6} M	5.40	14.9	4.00
8.4 × 10^{-6} M	5.90	17.3	4.20
2.4 × 10^{-5} M	11.6	35.5	5.10

[a] $[IrCl_6^{2-}]$ = 2.00 × 10^{-4} M, pH 1.10, and μ = 0.15 M at 25.0 °C. The concentration of reducing agent used in each series was held constant: [TU] = 8.50 × 10^{-3} M, [DT] = 1.00 × 10^{-2} M, and [IT] = 1.00 × 10^{-2} M.

Table III. Third-Order Rate Constants at Different Temperatures[a]

substrate	20.0 °C	25.0 °C	30.0 °C	35.0 °C
TU	327	388	486	566
DT	345	400	490	582
IT	242	300	389	471

[a] $[IrCl_6^{2-}]$ = 2.00 × 10^{-4} M, [reductant] = 2.42 × 10^{-3} to 1.67 × 10^{-2} M, μ = 0.15 M, and pH 1.10 M. The unit for k_3 is M^{-2} s^{-1}.

increased from 2.3 to 4.67. The three pH vs. log k_{obsd} plots in Figure 3 characterize the pH–rate profile observed. Reactions at pH 4–4.67 were conducted in acetate buffered solutions whereas for those at lower pH perchloric acid was added to adjust the hydrogen ion concentration.
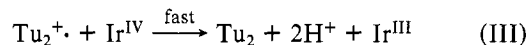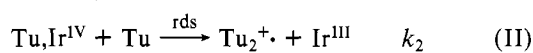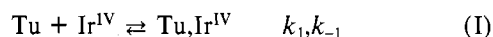
Copper Catalysis. The effect of Cu(II) ions on the reaction rate was determined by adding $CuSO_4$ to the $IrCl_6^{2-}$ solution before mixing with the thiourea solutions because Cu(II) is known to react with the thiourea with the formation of a Cu(I)–thiourea complex.[2a] The reaction conditions and results are summarized in Table II.

The data in Table II show that the reaction rate is enhanced considerably when $CuSO_4$ is added to the solution. Due to this catalysis, experiments have been carried out to examine how much trace Cu^{2+} impurities are in the reagents and the extent of catalyses in relation to the "uncatalyzed" reaction. By flame atomic absorption spectroscopy and kinetic studies based on the Cu^{2+} catalysis of the $IrCl_6^{2-}$ oxidation of CN^-, it is estimated that the upper limit of $[Cu^{2+}]$ in the reaction solutions is 6 × 10^{-7} M.[9]

Temperature Dependence. The effect of temperature on the rate of reaction was studied from 20.0 to 35.0 °C under the following reaction conditions: $[IrCl_6^{2-}]$ = 2.00 × 10^{-4} M, [thiourea] = 2.42 × 10^{-3} to 1.67 × 10^{-2} M, pH 1.10, and μ = 0.15 M. The values for k_3 at each temperature were obtained from the slopes of plots of k_{obsd} vs. [thiourea]^2 and are listed in Table III. From the k_3 values at each temperature the various activation parameters are calculated using the transition-state equation. The calculations were done using a computer program for the transition-state equation. The values of ΔH^*_3 for the three systems studied are 5.76 ± 0.30 (DT), 6.12 ± 0.33 (TU), and 7.51 ± 0.29 (IT) kcal mol^{-1}. The ΔS^*_3 values in units of cal deg^{-1} mol^{-1} are −27.3 ± 1.0 (DT), −26.1 ± 1.1 (TU), and −22.0 ± 1.0 (IT).

Discussion

The overall order for each of the three reactions being three indicates a rapid preequilibrium and an intermediate before the rate-determining step in the mechanism. Therefore, a reasonable mechanism which is consistent with the observed kinetics and stoichiometry is

$$Tu + Ir^{IV} \rightleftharpoons Tu,Ir^{IV} \qquad k_1, k_{-1} \qquad (I)$$

$$Tu,Ir^{IV} + Tu \xrightarrow{rds} Tu_2^+\cdot + Ir^{III} \qquad k_2 \qquad (II)$$

$$Tu_2^+\cdot + Ir^{IV} \xrightarrow{fast} Tu_2 + 2H^+ + Ir^{III} \qquad (III)$$

where Tu is the simplified representation for thiourea or the N,N'-dialkylthioureas, Ir^{IV} and Ir^{III} represent hexachloroiridate(IV) and -(III), and Tu_2 is the product, formamidine disulfide.

The usual steady-state derivation yielded the following derived rate law

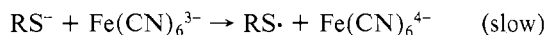$$\frac{-d[Ir^{IV}]}{dt} = \frac{2k_1k_2[Ir^{IV}][Tu]^2}{k_{-1} + k_2[Tu]} \qquad (4)$$

which corresponds to the observed kinetics of overall order of three when the following assumption is justified, $k_{-1} > k_2[Tu]$. The plots of k_{obsd} vs. $[Tu]^2$ are linear even when [Tu] is 0.10 M. Thus, under conditions of the present study one can equate $2k_1k_2/k_{-1}$ to k_3 of eq 3 with the assumption $k_{-1} > k_2[Tu]$. The mechanism postulated is analogous to the studies reported by Wilmarth and co-workers[10,11] on the oxidation of iodide and thiocyanate anions by $IrCl_6^{2-}$, $IrBr_6^{2-}$, and $Fe(bpy)_3^{3+}$ where dimeric radical ions of the substrates were invoked to account for the third-order path.

It is, of course, possible to propose an alternate mechanism to account for the kinetic behavior observed for the oxidation of the thioureas which would involve catalysis by trace metal ions in the solution. It is impossible to completely rule out this alternate mechanism. A likely candidate for such a pathway would be the Cu^{2+} ion which we show strongly accelerates the oxidation of the thiourea by $IrCl_6^{2-}$ (Table II). However, calculations based on a maximum concentration of Cu^{2+} of 6×10^{-7} M show that this ion cannot be responsible for the kinetic results.[9] At the most, only 10% (TU), 28% (DT), and 2% (IT) of the rate constants for the oxidation could be attributed to a Cu^{2+}-catalyzed pathway.

The rate–pH profile represents an interesting aspect of the present study which cannot be accounted for by a simple assumption that a monoprotonated species such as $NH_2CSNH_3^+$ exists at a pH of 1.10. In several previous works[1a–d] where the reactions were conducted at higher acid concentrations (0.17 M < [H⁺] < 3.70 M) the pK_a of thiourea in aqueous solutions was assumed to be equal to that reported in a dioxane–water mixture which is 2.03.[12] The pK_a values of thiourea and the N,N'-disubstituted thioureas in aqueous solutions of sulfuric acid have been determined spectrophotometrically to be -1.19[13] or -1.26[14] for TU, -1.32[13] for DT, and -1.9[13] or -2.59[15] for IT. Based on the present values of pK_as, it means that the thiourea is not significantly protonated at pH 1.10 as in this work. It is possible that the dissociation equilibrium involving
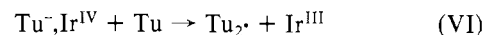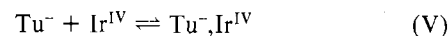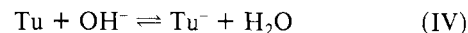
$$\underset{NH_2}{\overset{NH}{>}}C-S^-$$
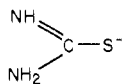
the anion of thiourea, could be involved in the reaction at higher pH. Another reasonable explanation of the pH effect on rate would be that the reaction is strongly base catalyzed. Such an argument is supported by the study of Wiberg and co-workers[16] on the $Fe(CN)_6^{3-}$ oxidation of 1-octanethiol where they postulated the following mechanism.

$$RSH + HO^- \rightleftharpoons RS^- + H_2O \qquad (fast)$$

$$RS^- + Fe(CN)_6^{3-} \rightarrow RS\cdot + Fe(CN)_6^{4-} \qquad (slow)$$

$$2RS\cdot \rightarrow RSSR \qquad (fast)$$

The disulfide cation radical in step II in the mechanism can certainly undergo further oxidation in step III to a dication of disulfide rather than the products. However, this dication is rather unstable at low acid concentration, and at pH greater than 1, it apparently breaks down to yield colloidal sulfur.[3,17] This is a reasonable possibility although we did not observe

any colloidal sulfur precipitation in our study. It is assumed that it deprotonates to yield the formamidine disulfide. No studies have been conducted at pH above 4.67 because of the rapid reduction of $IrCl_6^{2-}$ by OH^- in basic solution.[18] However, this reaction of $IrCl_6^{2-}$ with OH^- does not contribute to the reactions in this study as the pH range is well below that where this reaction is significant. A change in mechanism can also be ruled out at the higher pH since the kinetics of the reaction have been found to be second order in [TU] as well. Thus, the following base-catalyzed mechanism can be incorporated to explain the rate–pH behavior.
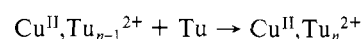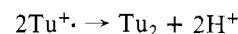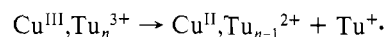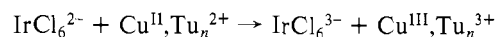
$$Tu + OH^- \rightleftharpoons Tu^- + H_2O \qquad (IV)$$

$$Tu^- + Ir^{IV} \rightleftharpoons Tu^-,Ir^{IV} \qquad (V)$$

$$Tu^-,Ir^{IV} + Tu \rightarrow Tu_2\cdot + Ir^{III} \qquad (VI)$$

$$Tu_2\cdot + Ir^{IV} \rightarrow Tu_2 + H^+ + Ir^{III} \qquad (VII)$$

Another plausible mechanism would involve step I, followed by

$$Tu,Ir^{IV} + Tu^- \rightarrow Tu_2\cdot + Ir^{III} \qquad (VIII)$$
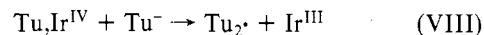
and step VII. Both mechanisms are consistent with the kinetic behavior and the results of oxidation of SCN^- and I^- by $IrCl_6^{2-}$.[10,11] The kinetics also rule out the possibility of the reaction of two thiourea anions. From Figure 3, it appears that there is no leveling of rate as pH is increased which makes it impossible to determine the pK_a of thioureas. There are also no pK_a values reported for the dissociation equilibrium of the thioureas.

The rate of oxidation of the substrates by $IrCl_6^{2-}$ follows the reactivity trend DT > TU > IT established by the metal aquo ions[1] and is in agreement with the order of inductive effect of the substituents.[19] The ΔH_3^* value is therefore expected for IT to be the highest and lowest for DT. However, no comparison can be made with those ΔH^*'s reported by other worker's since the kinetics of metal aquo ions as oxidants are different from the present systems. Moreover, these studies were at fairly high hydrogen ion concentrations and ionic strengths. It can be seen from the mechanistic steps I to III and the reduced form of eq 4 under the assumption of $k_2[TU] < k_{-1}$ that ΔH_3^* is a composite of $\Delta H_2^* + \Delta H_1°$. It is not known how $\Delta H_1°$ modifies the overall ΔH_3^* although the expected trend of variation in ΔH_2^* is observed for the three systems. Based on the inductive trends and the expected variation in ΔH^*, it can be concluded that the electron transfer site is at the sulfur atom.

Although a detailed kinetic study of the Cu(II)-catalyzed pathway was not carried out, a plausible mechanism can be proposed. The oxidation of thiourea by Cu(II) is a much slower process than the Cu(II)-catalyzed path studied here. This fact, coupled with the large value for the formation constant of the copper(II)–thiourea complex in water, suggests a mechanism in which the $IrCl_6^{2-}$ oxidized a copper(II)–thiourea complex to a copper(III)–thiourea complex which in turn decomposes to Cu(II) and the thiourea radical cation. Thus, a probable Cu(II)-catalyzed mechanism can be as follows:

$$IrCl_6^{2-} + Cu^{II},Tu_n^{2+} \rightarrow IrCl_6^{3-} + Cu^{III},Tu_n^{3+}$$

$$Cu^{III},Tu_n^{3+} \rightarrow Cu^{II},Tu_{n-1}^{2+} + Tu^+\cdot$$

$$2Tu^+\cdot \rightarrow Tu_2 + 2H^+$$

$$Cu^{II},Tu_{n-1}^{2+} + Tu \rightarrow Cu^{II},Tu_n^{2+}$$

Registry No. TU, 62-56-6; DT, 534-13-4; IT, 96-45-7; $IrCl_6^{2-}$, 16918-91-5; Cu^{2+}, 15158-11-9; $C_6H_{10}N_4S \cdot HCl$, 68213-04-7.

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Effects of Electron-Withdrawing Substituents on the Electrochemical Oxidation of Porphyrins

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Effects of β substitutions on the oxidation potentials of mesotetraphenylporphyrins are reported and compared with those observed in reduction of the same compounds. Remarkably, the magnitude of the redox potential shift induced by strong electron-withdrawing substituents (CN, NO_2) is different in oxidation from that in reduction. Typically, for the free-base tetraphenylporphyrin, the anodic shift resulting from four cyano substituents is +0.35 V in oxidation and +0.98 V in reduction. Also, at variance with results in reduction, the effects of β polysubstitution are nonadditive in oxidation, and for metalloporphyrins, these effects depend on the nonelectroactive central metal. These results may be interpreted by the existence of two sites for the electron transfer—the pyrrolic nitrogens in oxidation and the π-electron system in reduction.

A. Introduction

In nonaqueous media, the tetrapyrrolic macrocycle of the porphyrins is oxidized in successive monoelectronic steps[1-3] giving monocationic radicals and dications. The reduction of the tetrapyrrolic ring leads, by similar mechanisms, to monoanionic radicals and to dianions.[4,5] The half-wave potentials of these reversible reactions change with the electronegativity and the formal oxidation state of the central metal of the metalloporphyrins,[6] and they depend on the axial ligands[7,8] and the basicity of the tetrapyrrolic ring.[9] As a rule, the reduction of the porphyrin macrocycle becomes more difficult and its oxidation easier as the π-electron density increases. Recent studies have illustrated the variations of the electrochemical reactivity possible with changes in the chemical nature and the number of β and meso substituents on the porphyrin.[10-13]
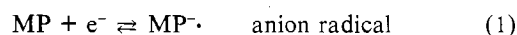
The study[10,11] of the effects of β substitutions on the electroreduction energies of porphyrins revealed that these effects may be dramatic and illustrated the possibility of synthesizing porphyrins with "tailor-made" reduction potentials over a wide range (up to 1 V). Also, with para substituents on the phenyls of tetraphenylporphyrins (TPP), shifts in the oxidation–reduction potentials have been measured and analyzed.[12,13] In this latter type of substitution, the observed effects are 5–6 times smaller than for pyrrole-substituted porphyrins.[10,14] The comparative papers published up to now

on the substituents' effects in porphyrins have reported analogous oxidation and reduction potential shifts.
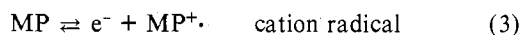
While this work is primarily devoted to the analysis of the effects of electron-withdrawing β substituents on the oxidation potentials of the porphyrin, their reduction, which had previously been measured on mercury, is also reported for platinum. These effects are analyzed by correlation involving the Hammett parameters, whose interest has been recalled in recent papers[15,16] and which are quite different for oxidation and reduction. On the basis of these differences, an interpretation is proposed for the influence of the β substituents on the electrochemical reactivity of porphyrins.

The two first electrode reactions of the porphyrins, in oxidation and in reduction, may be described as in reactions 1–4.

Reduction

$$MP + e^- \rightleftarrows MP^- \cdot \qquad \text{anion radical} \qquad (1)$$

$$MP^- \cdot + e^- \rightleftarrows MP^{2-} \qquad \text{dianion} \qquad (2)$$

Oxidation

$$MP \rightleftarrows e^- + MP^+ \cdot \qquad \text{cation radical} \qquad (3)$$

$$MP^+ \cdot \rightleftarrows e^- + MP^{2+} \qquad \text{dication} \qquad (4)$$

In this reaction scheme, M is $(H)_2$ or the central metal in the metalloporphyrin, the central metal is chosen to be nonelectroactive (Cu^{II}, Pd^{II}, Zn^{II}), and P is the ligand por-