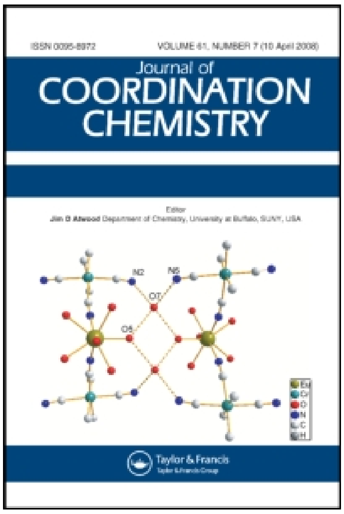

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Po, H. N. , Lo, C. F. , Jones, N. K. , Galuska, A. A. and Eran, H.(1981) 'GENERAL MECHANISM FOR ONE ELECTRON OXIDATION OF HETEROCYCLIC THIOAMIDES BY Ir(IV) AND Fe(III) COMPLEXES', Journal of Coordination Chemistry, 11: 3, 163 — 169

To link to this Article: DOI: 10.1080/00958978108079064

URL: http://dx.doi.org/10.1080/00958978108079064

J. Coord. Chem., 1981, Vol. 11, pp. 163–169
0095-8972/81/1103-0163 $06.50/0

GENERAL MECHANISM FOR ONE ELECTRON OXIDATION OF HETEROCYCLIC THIOAMIDES BY Ir(IV) AND Fe(III) COMPLEXES

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(Received March 24, 1981; in final form June 18, 1981)

The kinetics of the oxidation of 2-thiouracil (TU) by $Fe(bpy)_3^{3+}$ follows a second-order rate law while the oxidation of 4-methyl-2-thiopyrimidine (MTP) and 4,6-dimethyl-2-thiopyrimidine (DMTP) by $IrCl_6^{2-}$ obeys a two-term rate law, a third-order and a second-order reaction. The k_{II} at 25.0°C, $\mu = 0.10$ M and pH = 2.3 for TU oxidation is 4.14 ± 0.17 M^{-1} s^{-1}. The k_{II} and k_{III} at 25.0°C, $\mu = 0.10$ M and pH = 2.1 are 1.65 M^{-1} s^{-1} and 2.05×10^3 M^{-2} s^{-1} for $IrCl_6^{2-}$ + DMPT and 5.5 M^{-1} s^{-1} and 3.50×10^3 M^{-2} s^{-1} for $IrCl_6^{2-}$ + MTP. Rate-pH profile observed for these reactions are accounted for by the acid-base equilibria of the thiols in solution and the greater reactivity of the mercaptide anions. The mercaptide anions react with the oxidants 10^4 times faster than the neutral thiols. A general mechanism has been postulated to account for the two-term rate law. Activation parameters are also reported at low pH for all three systems.

INTRODUCTION

Widely distributed in enzymes, hormones, pharmacologically active polypeptides and other proteins are the sulfhydryl (-SH) and disulfide (-SS-) groups.[1] Biochemical oxidizing agents that have less negative redox potential than the -SH, such as flavin, cytochrome *C*, dehydroxylascorbic acid, quinones. amino acids, and fumarate can remove electrons from the thiols and oxidize them to disulfides in living cells.[2] Since sulfur can have valences varying from minus two to plus six, oxidation products other than disulfide, such as sulfenic acid, sulfinic acid, and sulfonic acid are possible. Many interesting synthetic procedures have been developed to prepare the wide variety of oxygenated organosulfur compounds.[3]

The kinetics and mechanisms of oxidation of many thiols such as thioureas,[4] 2-mercaptoethanol,[5] 2-mercaptosuccinic acid,[6] thiolmalic acid,[7] 3-mercaptopropionic acid,[8] some alkyl-, benzyl-, and arylthiols,[9] 2-thiopyrimidine,[10] and 2-thiouracil[10] have been reported recently. The oxidants include a large variety of metal ions and metal complexes. In many instances, thiyl radicals generation has been postulated and observed in the oxidation of thiols.[11]

In this study, we have investigated the one electron oxidation kinetics of 2-thiouracil by tris(bipyridyl)-iron(III) ion, and 4-methyl-2-thiopyrimidine and 4,6-dimethyl-2-thiopyrimidine by hexachloroiridate(IV) ion in aqueous solutions. The iron(III) and iridium(IV) complexes are relatively substitution inert as well as powerful oxidizing agents. They are also selected to avoid complication from the substitution rate-controlled reactions when metal aquo cations are used. Because of this extension of our previous work,[10] a general mechanism is postulated to account for the one electron oxidation of the heterocyclic thioamides.

EXPERIMENTAL SECTION

Materials

Potassium hexachloroiridate(IV) was from Alfa Chemicals and was used as supplied. Tris(bipyridine)-iron(III) perchlorate was prepared according to Sutin and Gordon.[12] The thiol compounds, 2-thiouracil (TU), 4-methyl-2-thiopyrimidine hydrochloride (MTP), and 4,6-dimethyl-2-thiopyrimidine (DMTP) were recrystallized twice from aqueous-ethanol solutions under mild conditions. The purity of the recrystallized compounds were verified using melting points and uv-vis spectroscopy techniques. Sodium perchlorate, used to maintain ionic strength, was prepared from perchloric acid neutralization of sodium carbonate. Sodium dihydrogen phosphate and sodium acetate were used to prepare several of the buffer solutions in the pH kinetic studies. Triple distilled water was used to prepare all reaction solutions.

Kinetic Studies

The oxidation of the thiol compounds were monitored with either a Durrum-Gibson or an Aminco-Morrow stopped-flow spectrophotometer. Those reactions with $IrCl_6^{2-}$ as the oxidant were monitored at 487 nm while reactions with $Fe(bpy)_3^{3+}$ were studied at 522 nm. All the reaction solutions were prepared just prior to each kinetic run to avoid decomposition of the reactants, particularly the oxidizing agents. They were placed in a thermostatted water bath at the reaction temperature for at least 15 minutes before each run. The stopped-flow apparatus was also thermostatted with circulating water from the bath. Similar precautions were taken for those reactions that were slow enough to be followed in the Cary 14 spectrophotometer. Pseudo-first-order conditions prevailed throughout this study with the reductant concentration always in tenfold or more excess over the oxidant. Plots of log $(A_t - A_\infty)$ versus time were linear. The pseudo-first-order rate constants, k_{obs}, were calculated from the slopes of these plots.

Stoichiometry and Products Identification

The stoichiometry of the oxidation of 2-thiopyrimidine and 2-thiouracil by IrX_6^{2-} complexes was determined previously to be 1 : 1.[10] For the substituted 2-thiopyrimidine, in particular, the stoichiometry of 4-methyl-2-thiopyrimidine oxidation by $IrCl_6^{2-}$ was performed in natural pH aqueous solutions with $[MTP] = 2.50 \times 10^{-3}$ to 1.25×10^{-2} M and $[IrCl_6^{2-}] = 1.25 \times 10^{-3}$ to 2.50×10^{-4} M, an average value of $\Delta[IrCl_6^{2-}]/\Delta[MTP] = 1.06$ was obtained. Similarly, a one to one stoichiometry was obtained for the oxidation of 2-thiouracil by $Fe(bpy)_3^{3+}$. When excess oxidant was used, further oxidation of the disulfide formed was observed in the MTP + $IrCl_6^{2-}$ system as well as in the TU + $Fe(bpy)_3^{3+}$ reaction. This variable stoichiometry was observed previously for the oxidation of 2-thiopyrimidine by IrX_6^{2-} (X = Cl, Br). This, therefore, mitigated that the kinetics be done with the concentration of the thiol compounds always be in excess in order to maintain the simple 1 : 1 stoichiometry. Spectral analysis of the inorganic products produced gave $IrCl_6^{3-}$ and $Fe(bpy)_3^{2+}$. The elemental analysis of the organic product isolated for the 4-methyl-2-thiopyrimidine oxidation agreed with the disulfide. Melting point and uv-vis spectral of the product were also taken and compared with the disulfide synthesized by I_2 oxidation.[13] The stoichiometry of the redox reaction can, therefore, be represented by eq. (1).

$$2\ RSH + 2\ IrCl_6^{2-}\ (\text{or } 2\ Fe(bpy)_3^{3+}) \rightarrow RSSR + 2H^+ + 2\ IrCl_6^{3-}\ (\text{or } 2\ Fe(bpy)_3^{2+}) \qquad (1)$$

RESULTS AND DISCUSSION

Oxidation of 2-Thiouracil by $Fe(bpy)_3^{3+}$

Pseudo-first-order kinetics carried out with (TU) in excess, constant pH, and ionic strength of 0.10 M gave linear log $(A_t - A_\infty)$ *vs* time plots. The k_{obs} values calculated from the slopes of these first-order plots are listed in Table I. The reaction was first-order in (TU) and in $[Fe(bpy)_3^{3+}]$ which was corroborated in the constancy of k_{II}, the second-order rate constant. The average k_{II} calculated for $[Fe(bpy)_3^{3+}] = 0.45 \times 10^{-4}$ to 2.57×10^{-4} M, [TU] = (1.02–3.38) 10^{-3} M,

TABLE I
Concentration dependence study on 2-thiouracil + $Fe(bpy)_3^{3+}$.[a]

$10^4[Fe(bpy)_3^{3+}]$, M	$10^3 \times$ [TU], M	$10^3 \times k_{obs}$, sec^{-1}	k_{II}, M^{-1} s^{-1}
1.00	1.02	4.39	4.30
1.00	2.01	8.58	4.27
1.00	2.53	11.5	4.55
1.00	3.11	13.1	4.21
1.00	3.38	14.1	4.17
2.57	2.54	10.1	3.98
2.50	2.54	9.81	3.86
1.50	2.54	10.1	3.98
0.99	2.54	10.6	4.17
0.45	2.54	9.95	3.92
			average: 4.14 ± .17

[a] pH = 2.3, and at 25.0°C.

pH = 2.3, μ = 1.10 M and at 25.0°C is 4.14 ± .17 M^{-1} sec^{-1}. The rate law for the above reaction is, therefore,

$$-d\ln[Fe(bpy)_3^{3+}]/dt = k_{obs} = k_{II}[TU] \quad (2)$$

where k_{II} is the second-order rate constant at low pH.

Oxidation of Substituted 2-Thiopyrimidines by $IrCl_6^{2-}$

Reactions between MTP or DMTP with $IrCl_6^{2-}$ were carried out at excess thiol concentration to ensure pseudo-first-order conditions. At constant pH = 2.1, μ = 0.10 M, [thiol] = 3.00×10^{-3} M, and with $[IrCl_6^{2-}]$ varied from 3.0×10^{-5} to 2.00×10^{-4} M the constancy of the pseudo-first-order rate constants k_{obs} as a function of $[IrCl_6^{2-}]$ was confirmed. The values of k_{obs} at 25.0°C for MTP + $IrCl_6^{2-}$ and DMTP + $IrCl_6^{2-}$ are 3.47×10^{-2} M^{-1} s^{-1} and 1.95×10^{-2} M^{-1} s^{-1}, respectively. Thiol concentration dependence studies were also conducted at pH = 2.1, μ = 0.10 M by varying the concentration of thiol at constant $[IrCl_6^{2-}]$. Plots of k_{obs} versus [thiol] do not show the expected linearity observed in previous studies. The deviation from linearity was observed to occur at higher concentrations of thiol used in the experiment. In previous work, due to the limited solubility of 2-thiopyrimidine and 2-thiouracil in water, studies were limited to lower concentrations of thiols. This prevented the observation of the curvature in the k_{obs} *vs* [thiol] plot. In the present study, because of the high solubility of 4-methyl-2-thiopyrimidine hydrochloride in water, the kinetic measurement was extended upward to 1.60×10^{-2} M to confirm and establish this departure from linearity of the rate-concentration plot.

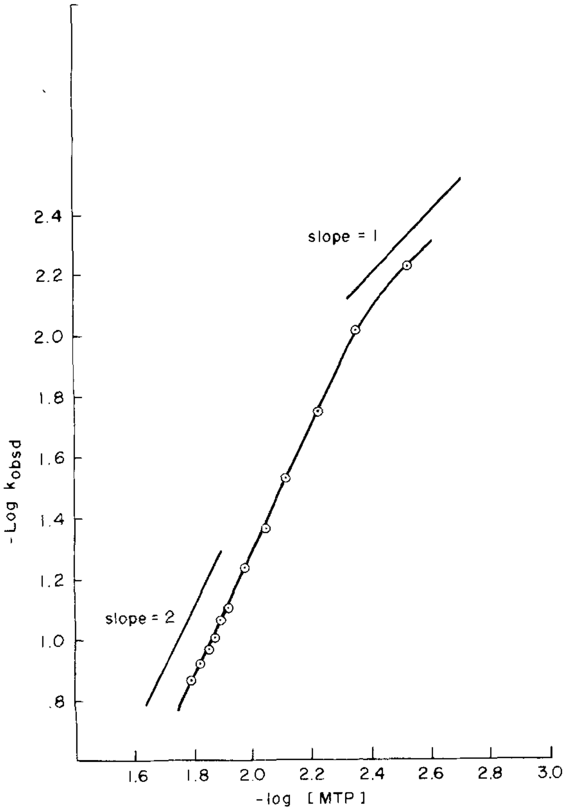

FIGURE 1 Log k_{obs} *vs* log [MTP] at pH 1.1, μ = .15 M, $[IrCl_6^{2-}]$ = 2.00×10^{-4} M and 25.0°C.

A series of reactions at constant $[IrCl_6^{2-}]$ = 2.00×10^{-4} M, pH = 1.10, μ = 0.15 M, and 25.0°C with [MTP] = 1.60×10^{-2} M to 3.00×10^{-3} M was carried out. The data obtained for this reaction were plotted as log [MTP] versus log k_{obs} and shown in Figure 1. Two slopes are obtained, a slope of unity at lower [MTP] and a gradual increase of the slope to two when the [MTP] exceeded 4.5×10^{-3} M. The result suggests that the reaction kinetic has a first-order and a second-order dependence in [MTP]. Therefore, a two-term rate law can be written to show the general kinetic behavior for the one electron oxidation of these heterocyclic thioamides as shown in eq. (3).

$$-d[IrCl_6^{2-}]/dt = k_{obs}[IrCl_6^{2-}] = \{k_{II} + k_{III}[RSH]\}[IrCl_6^{2-}][RSH] \quad (3)$$

The k_{II} and k_{III} are the second- and third-order rate constants at constant pH. Two-term rate laws are not unusual and have been reported for one electron oxidation reactions involving anions such as I^- and SCN^- by the same oxidants.[14]

Graphical method demonstrating the [thiol] dependence in plots of k_{obs}/[thiol] versus [thiol] is shown in Figures 2 and 3 for the oxidation of MTP and DMTP at four temperatures. The intercepts and slopes of these plots yielded values for k_{II} and k_{III}. These reactions were carried out under the following conditions: pH = 2.1, μ = 0.10 M, $[IrCl_6^{2-}]$ = 5.00×10^{-5} M, [MTP] = 3.10×10^{-4} to 7.00×10^{-3} M and [DMTP] = 6.06×10^{-4} to 3.01×10^{-3} M. Table II lists values of k_{II} and k_{III} obtained for MTP + $IrCl_6^{2-}$ and DMTP + $IrCl_6^{2-}$ at 25°, 30°, 35°, and 40°C.

pH Rate Dependence

The kinetics of the oxidation of TU by $Fe(bpy)_3^{3+}$ and MTP and DMTP by $IrCl_6^{2-}$ have been observed to follow a kinetic pH rate profile reported earlier for the oxidation of thioureas,[4] thiouracil, and thiopyrimidine.[10] A plot of the pH kinetic behavior for the oxidation of MTP by $IrCl_6^{2-}$ is shown in Figure 4. As depicted in the graph, the rate of oxidation is fairly slow at low pH

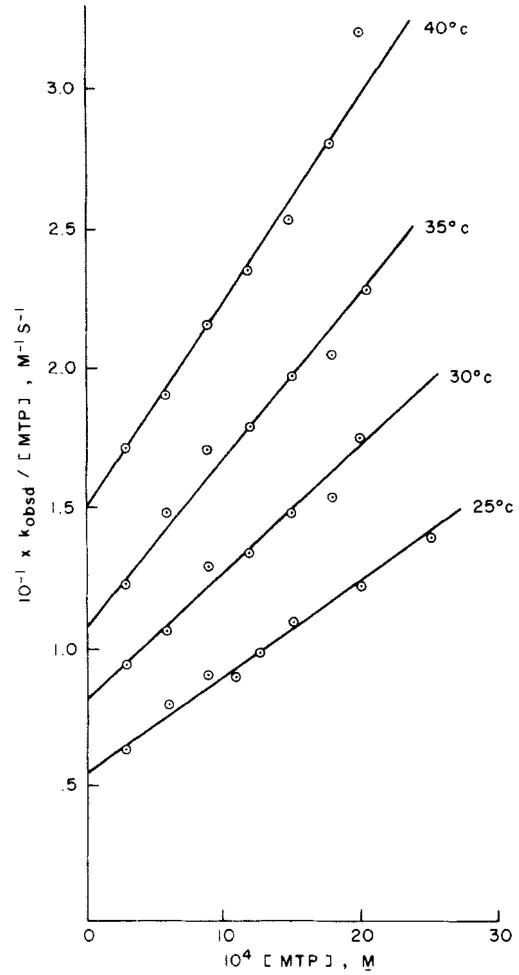

FIGURE 2 Plots of $k_{obs}/[MTP]$ vs [MTP] at various temperatures. $[IrCl_6^{2-}] = 5.0 \times 10^{-5}$ M, pH = 2.1 and μ = 0.10 M.

TABLE II
Temperature dependence rate data for the $IrCl_2^{2-}$ oxidation of MTP and DMTP.[a]

	25.0°C	30.0°C	35.0°C	40.0°C
DMTP + $IrCl_6^{2-}$:				
k_{II}, $M^{-1}\,s^{-1}$	1.65	2.76	4.50	6.70
$10^{-3}\,k_{III}$, $M^{-2}\,s^{-1}$	2.05	2.69	3.60	4.50
MTP + $IrCl_6^{2-}$:				
k_{II}, $M^{-1}\,s^{-1}$	5.5	8.3	11.4	14.4
$10^{-3}\,k_{III}$, $M^{-2}\,s^{-1}$	3.50	4.37	5.54	8.05

[a] pH = 2.1 and μ = 0.10 M.

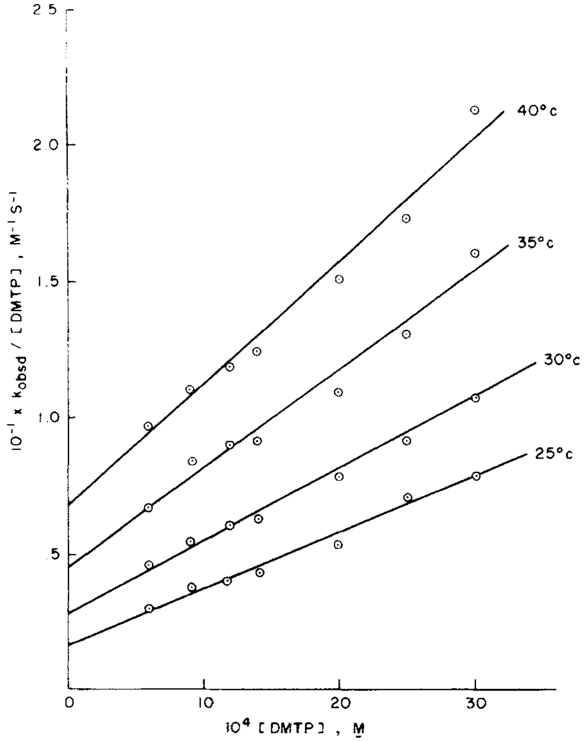

FIGURE 3 Plots of $k_{obs}/[DMTP]$ vs [DMTP] at various temperatures. $[IrCl_6^{2-}] = 5.0 \times 10^{-5}$ M, pH 2.1, and μ = 0.10 M.

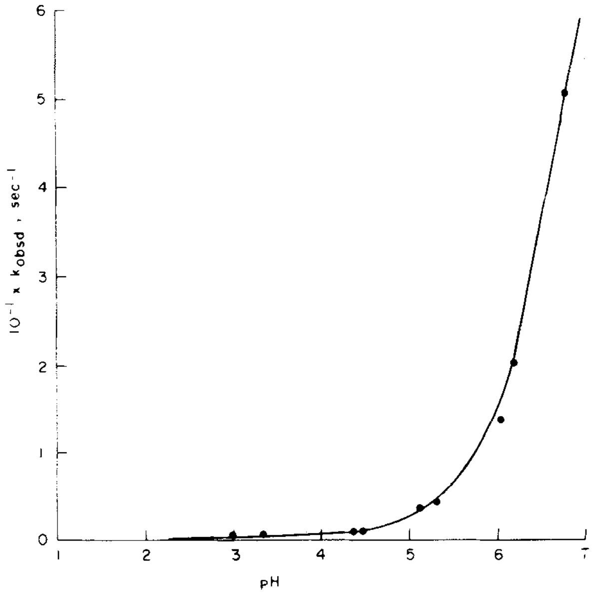

FIGURE 4 pH-Rate Profile of $IrCl_6^{2-}$ + MTP Reaction. $[IrCl_6^{2-}] = 2.00 \times 10^{-4}$ M, $[MTP] = 1.00 \times 10^{-2}$ and 25.0°C.

(2–3.6), but increases sharply when the pH is raised above 3.6. Data for the oxidation of TU by $Fe(bpy)_3^{3+}$ and DMTP by $IrCl_6^{2-}$ are presented in Tables III and IV. They both show the same trend as the MTP oxidation. When plots of log k_{obs} versus pH are constructed for the various redox systems investigated, slopes of unity or near unity are obtained, suggesting that these reactions are inversely proportional to the hydrogen ion concentration.

A normal pH-rate behavior involving protonated and unprotonated reactive species over a certain pH span will certainly yield a sigmoidal-shaped plot. However, due to the rapid reduction of $IrCl_6^{2-}$ [15] and $Fe(bpy)_3^{3+}$ by OH^- in basic solutions,[16] no reactions were conducted near or above pH 7. This is one of the reasons that no leveling off effect has been reported and that a partial pH-rate profile prevailed in all cases.

TABLE III

pH Dependence rate data for the oxidation of 2-thiouracil by $[Fe(bpy)_3^{3+}]$.[a]

pH	$10^2 \times k_{obs}$, sec^{-1}	k_{II}, $M^{-1} sec^{-1}$
2.07	0.56	3.68
2.60	0.71	4.59
3.07	1.20	7.79
3.30	1.42	8.88
3.56	1.47	9.80
3.82	1.67	11.2
4.01	3.00	19.7
4.34	6.50	42.7
4.66	20.3	133
4.84	35.7	232
5.02	57.5	376
5.35	111.0	729

[a] $[Fe(bpy)_3^{3+}] = (1.50–1.60) \times 10^{-3}$ M, [TU] = $(1.40–1.60) \times 10^{-4}$ M, $\mu = 0.10$ M and at 25.0°C.

TABLE IV

pH Dependence rate data for the oxidation of 4,6-dimethyl-2-thiopyrimidine by $IrCl_6^{2-}$.[a]

pH	$10^3 \times$ [DMTP], M	$10^2 \times k_{obs}$, sec^{-1}
2.12	2.00	0.70
3.19	2.00	1.54
4.63	2.00	7.41
6.76	2.00	722
6.76	3.00	1120

[a] $[IrCl_6^{2-}] = 5.00 \times 10^{-5}$ M, $\mu = 0.10$ M, and at 25.0°C.

General Mechanistic Scheme

A general mechanistic scheme which is consistent with the observed kinetics and stoichiometry is shown by eqs. (4) to (7).

$$Ir(IV) + RSH \rightleftharpoons Ir(III) + RS\cdot + H^+ \qquad k_2, k_{-2} \quad (4)$$

$$Ir(IV) + 2RSH \rightleftharpoons Ir(III) + (RS)_2\cdot + 2H^+ \qquad k_3, k_{-3} \quad (5)$$

$$Ir(IV) + (RS)_2^{\bar{\cdot}} \rightleftharpoons Ir(III) + (RS)_2 \qquad k_4, k_{-4} \quad (6)$$

$$RS\cdot + RSH \rightleftharpoons (RS)_2^{\bar{\cdot}} + H^+ \qquad k_5, k_{-5} \quad (7)$$

Applying the steady-state approximation to the mechanism and with the following assumptions:

$k_{-3}[Ir(III)][H^+]^2 \ll k_4[Ir(IV)]$, $k_{-2}[Ir(III)][H^+] \ll k_5[RSH]$, and $k_{-2}k_{-5}[Ir(III)][H^+]^2 \ll k_4k_5[RSH][Ir(IV)]$, a rate law (equation 8) is derived.

$$-d\frac{[Ir(IV)]}{dt} = 2[Ir(IV)][RSH]\{k_2 + k_3[RSH]\} \quad (8)$$

where $k_{II} = 2k_2$ and $k_{III} = 2k_3$. Thiyl radicals of 2-thiouracil and 2-thiopyrimidine have been reported in studies involving biological systems.[17] The k_2 path reasonably accounts for the second-order term in the rate law, eq. (8). In those reactions where only this term is reported as in the TU + $Fe(bpy)_3^{3+}$ reaction, the k_2 path is the preferred reaction step over the k_3 path where high concentrations of RSH is required. A mechanism involving the dimerization of RS· was ruled out because RS· probably will much more quickly react to form $(RS)_2^{\bar{\cdot}}$ in the presence of high RSH concentration.

An original intimate mechanism which has been proposed to account for the I^- and SCN^- oxidation by IrX_6^{2-} (X = Cl, Br) details the k_2 and k_3 steps with several ion pairs equilibria scheme.[14] Such an intimate mechanism is adaptable to the present situation and would be consistent with the observed kinetics.

The interesting pH-rate kinetics in the present study can be accounted for by the acid-base equilibrium of RSH in aqueous solution and parallel reaction pathways involving the more reactive RS^- anion with Ir(IV). Thus, the following anion oxidation steps can be incorporated to explain the pH-rate behavior.

$$RSH \rightleftharpoons RS^- + H^+ \qquad K_1 \quad (9)$$

$$Ir(IV) + RS^- \rightleftharpoons Ir(III) + RS\cdot \qquad k'_2, k'_{-2} \quad (10)$$

$$Ir(IV) + 2RS^- \rightleftharpoons Ir(III) + (RS)_2^{\bar{\cdot}} \qquad k'_3, k'_{-3} \quad (11)$$

TABLE V
Reactivity of the thiols and their corresponding anions.[a]

System	k_2, $\text{M}^{-1}\ \text{s}^{-1}$	k'_2, $\text{M}^{-1}\ \text{s}^{-1}$	k_3, $\text{M}^{-2}\ \text{s}^{-1}$	k'_3, $\text{M}^{-2}\ \text{s}^{-1}$
$IrCl_6^{2-}$ + TU[b]	0.094	2.3×10^3	–	–
$IrCl_6^{2-}$ + TP[b]	1.65	8.0×10^4	–	–
$IrCl_6^{2-}$ + DMTP	0.83	1.0×10^5	1×10^3	10^7
$IrCl_6^{2-}$ + MTP	2.75	1.0×10^5	2×10^3	10^7
$Fe(bpy)_3^{3+}$ + TU	2.07	2×10^4	–	–

[a] $\mu = 0.10$ M, 25°C.

[b] Ref. 10; The values given in the reference are corrected by multiplying by a factor of 1/2. This is due to the rate law derived for the general mechanism proposed and $k_{II} = 2k_2$ and $k_{III} = 2k_3$.

where k'_2 and k'_3 are the second-order and third-order rate constants for the oxidation of the mercaptide ions at high pH.

The pK_as'[18] of TU, MTP, and DMTP are 7.74, 8.1, and 8.5, respectively. Therefore, at fairly low pH where most of the kinetics are measured, only eqs. (4)–(7) prevail, since neutral thiols are the reactive species. The values of pK'_as together with the nature of the pH-rate kinetics do strongly indicate that the mercaptide anions are far more reactive than the neutral thiols. From the rate data obtained at higher pH as a function of thiol concentrations and the rate-pH equation developed by Wilkins,[19] values of k'_2 and k_2 can be calculated from known k_{II}, pK_a, and pH. These values are tabulated in the reactivity table, Table V, for comparison with previous data. Similar calculations can be performed for k'_3 and k_3, however, with lesser accuracy.

Comparison of k'_2 and k_2 for the five systems studied supports the earlier prediction that the mercaptide anions are about 10^4 times more reactive than the neutral thiols. The order of reactivity (k_2) of the various thiols with $IrCl_6^{2-}$ is as follows: MTP > TP > DMTP ≫ TU. The mercaptide anions oxidation (k'_2) follows almost a similar order; MTP ~ DMTP > TP > TU only with the position of TP and DMTP reversed. It is expected that the anions of MTP and DMTP with electron donating substituents on the ring will react faster than their parent neutral molecules since electron density at the reaction site, the S atom, has been increased. However, in the case of neutral thiols, steric hindrance of the methyl groups on DMTP could probably be the reason for the lower reactivity of DMTP when compared to TP. Nevertheless, only a factor of two in k_2 is observed between TP and DMTP. The 2-thiouracil compound, as expected, reacts the most sluggishly because of the presence of the electron-withdrawing substituent on the ring. Comparison of the third-order k'_3 and k_3 show that the anions MTP and DMTP are at least 10^4 times more reactive than their natural parent thiols. Between $Fe(bpy)_3^{3+}$ and $IrCl_6^{2-}$, it is not surprising that $Fe(bpy)_3^{3+}$ oxidation of TU is twenty to forty times faster than that of $IrCl_6^{2-}$. This can be attributed to $Fe(bpy)_3^{3+}$ being a better oxidant than $IrCl_6^{2-}$ and also to its positive three charge.

TABLE VI
Activation parameters at pH 2.1.

System	$\Delta H^{\ddagger}$, Kcal/mole	$\Delta S^{\ddagger}$, e.u.	$\Delta G^{\ddagger}$, Kcal/mole
a) *Second-Order Term*			
$IrCl_6^{2-}$ + TU[a]	10.1	−27.8	18.4
$IrCl_6^{2-}$ + TP[a]	7.5	−31.8	16.7
$IrCl_6^{2-}$ + DMTP	15.9	−4.1	17.1
$IrCl_6^{2-}$ + MTP	11.0	−18.1	16.4
$Fe(bpy)_3^{3+}$ + TU	10.5	−21.7	16.9
b) *Third-Order Term*			
$IrCl_6^{2-}$ + DMTP	9.8	−10.6	12.9
$IrCl_6^{2-}$ + MTP	8.4	−14.3	12.6

[a] Ref. 10.

Activation Parameters

The overall $\Delta G^{\ddagger}$ at pH 2.1 shown in Table VI shows that the order of reactivity of thiols with $IrCl_6^{2-}$ agrees with the order established from the reactivity table. We have earlier attributed to steric effect the differences in reactivity between TP and DMTP. This is supported by the $\Delta S^{\ddagger}$ values (-31.0 e.u. *vs* -4.1 e.u.) obtained in this study. It appears that in this series of studies $\Delta S^{\ddagger}$ plays a significant role in the kinetics of one electron oxidation of heterocyclic thioamides. Since no temperature dependence work was performed at high pH, activation parameters for the mercaptide anions oxidation are not available. However, it can be expected that the order of reactivity of the mercaptide anions should be the same: MTP $\sim$ DMTP $>$ TP $>$ TU.

ACKNOWLEDGEMENT

Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. Henry N. Po wishes to thank the University Reseach Committee for a research grant-in-aid award.

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