

The kinetics of the oxidation of thiourea by 12-tungstocobaltate(III) ion: evidence for anionic, neutral and protonated thiourea species in acetic acid–acetate buffer and perchloric acid solution

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The kinetics of the redox reaction between 12-tungstocobaltate(III) ion, $[\text{Co(III)W}]^{5-}$, and thiourea is studied in acetic acid–acetate buffered solutions ($3.4 \leq \text{pH} \leq 5.6$), and dilute perchloric acid solution. The reaction in buffered solution is first order both in $[\text{Co(III)W}]^{5-}$ and low $[\text{H}_2\text{NCSNH}_2]$. A simultaneous first- and second order dependence is observed at high $[\text{H}_2\text{NCSNH}_2]$. The rate is independent of $\text{pH} \leq 4.6$ due to the participation of H_2NCSNH_2 . In solutions of $\text{pH} \geq 4.6$, the rate increases with the pH due to the dissociation of H_2NCSNH_2 to the reactive H_2NCSNH^- ion. In dilute perchloric acid solutions the rate increases with increasing $[\text{H}^+]$ due to the participation of protonated $\text{NH}_2\text{C}^+\text{SHNH}_2$ species. The seat of the reaction is thought to be the enolic S atom (not protonated S) rather than the protonated nitrogen of the NH_2 group as in the oxidations of NH_2OH , H_2NNH_2 and N_3H where the rate is retarded by the increase in $[\text{H}^+]$. The acid dissociation constant, K_a , of protonated $\text{NH}_2\text{C}^+\text{SHNH}_2$ is estimated to be $0.048 \text{ mol dm}^{-3}$ at 40°C . The Marcus theory is used to estimate the self-exchange rate (k_{22}) of the $\text{H}_2\text{NCSNH}_2^-$ ($\text{H}_2\text{N})_2\text{CSSC}(\text{NH}_2)_2$ couple. The estimated k_{22} is $2.44 \times 10^{-10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The low value is attributed to the stable dimeric $(\text{H}_2\text{N})_2\text{CSSC}(\text{NH}_2)_2$ species.

Introduction

In the oxidation of thiolactic acid,¹ hydroxylamine,² hydrazine³ and azide⁴ by 12-tungstocobaltate(III) ($[\text{Co(III)W}]^{5-}$) the species $\text{CH}_3\text{CH}(\text{SH})\text{COO}^-$, NH_2OH , N_2H_4 and N_3^- ion, having a lone pair of electron, happened to be more reactive than the species $\text{CH}_3\text{CH}(\text{SH})\text{COOH}$, NH_3OH^+ , N_2H_5^+ and HN_3 that are devoid of such a pair. The Keggin structure of $[\text{Co(III)W}]^{5-}$ ion⁵ precluded an inner-sphere mechanism since the central Co(III) atom is strongly shielded. Hence, the oxidations were treated as outer-sphere supported by the application of the Marcus cross relation.⁶

Thiourea with a lone pair of electrons on S atom is the obvious choice to further substantiate the high reactivity of the species with lone pair of electrons. The extremely slow oxidation of urea was not attempted. The Ce(IV) ,⁷ Co(III) ,⁸ $\text{Mn(III)}_{\text{aq}}$,⁹ Cu(II) complexes,¹⁰ H_2O_2 ,¹¹ iodate,¹² Os(VIII) ,¹³ Fe(III) ,¹⁴ Ti(VI) ,¹⁵ $[\text{Mn}(\text{cdta})]^-$,¹⁶ ($\text{H}_4\text{cdta} = \text{trans-cyclohexane-1,2-diamine-}N,N',N',N'\text{-tetraacetic acid}$) oxidations were considered inner-sphere; those by IrCl_6^{2-} ion,¹⁷ and $[\text{Co(III)W}]^{5-}$ ions¹⁸ were found outer-sphere.

The study was under taken to reinvestigate the effects of $[\text{H}^+]$ and the ionic strength on the observed rate and, if possible, to deduce the self-exchange rate of $2\text{H}_2\text{NCSNH}_2-(\text{H}_2\text{N})_2\text{CSSC}(\text{NH}_2)_2$ couple using Marcus theory.⁶

The present study in acetate–acetic acid buffer and perchloric acid medium confirms some of the previous observations and presents a new insight into the rate law. The rate law is a combination of two terms; a first-order in $[\text{thiourea}]$ ($0.005\text{--}0.1 \text{ mol dm}^{-3}$) and a second order in $[\text{thiourea}]$ ($>0.1 \text{ mol dm}^{-3}$) against first-order dependence in H_2NCSNH_2 reported in the previous study.¹⁸ The rate was independent of pH (3.40 to 4.60) but increased at high pH in the range (4.60 to 5.57). The rate measurements at $[\text{HClO}_4] \leq 0.1 \text{ mol dm}^{-3}$ exhibited a linear dependence on $[\text{H}^+]$ whereas a second order dependence in $[\text{H}^+]$ was noted for $[\text{HClO}_4] > 0.1 \text{ mol dm}^{-3}$. However, the appropriate correlation between k_{obs} and $[\text{H}^+]$ for the entire range of investigated $[\text{H}^+]$ is discussed later.

Experimental

The thiourea sample was recrystallised from warm 20% v/v aqueous ethanol.¹⁰ The purity of the recrystallised sample was checked by determining its melting point (found 181°C ; lit. $180\text{--}182^\circ\text{C}$ ¹⁰). The solutions were prepared immediately before use to avoid complications due to slow decomposition reactions occurring in the presence of perchloric acid.⁹ $\text{K}_5[\text{Co(III)W}]^{5-}$ was prepared by the method described by Baker and McCutcheon.¹⁹ Acids were suitably diluted and standardised against a standard alkali solution. The sodium acetate–acetic acid buffer solutions (0.2 mol dm^{-3}) of different pH were prepared as described,²⁰ and the pH s were checked with a Systronics 335 digital pH meter.

Rate measurement

The disappearance of $[\text{Co(III)W}]^{5-}$ was measured at 390 nm on a Union Giken RA-401 stopped flow spectrophotometer under pseudo-first-order conditions ($[\text{H}_2\text{NCSNH}_2] \gg [\text{Co(III)W}^{5-}]$) at constant ionic strength (0.5 mol dm^{-3} , LiClO_4) unless stated otherwise. The k_{obs} , the pseudo-first-order rate parameter, were calculated with the interfaced microcomputer programmed for collecting and analysing the data by averaging the volt–time curves. The usual first order plots were linear for more than three half-lives and the reproducibility of k_{obs} was within $\pm 5\%$. There was no erratic increase in the absorbance of the reaction solution in the stopped flow cell reported in the oxidation of hydrogen peroxide ($\text{pH} > 1$) caused by the breakdown of the oxidation product formamidine disulfide ion to colloidal sulfur.¹¹ The effect of the variation of $[\text{H}_2\text{NCSNH}_2]$ on rate at pH 4.45 is investigated at several temperatures. The effect of variation of pH and $[\text{H}^+]$ are investigated at one temperature with high $[\text{H}_2\text{NCSNH}_2]$ (0.15 mol dm^{-3}).

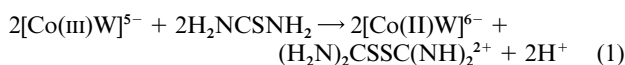
Stoichiometry

The stoichiometry of the reaction was estimated at 390 nm with different concentration ratios of $[\text{Co(III)W}]^{5-}$ and H_2NCSNH_2

Table 1 The dependence of k_{obs} on [thiourea] at different temperatures. $10^4 [\text{Co(III)W}]^{5-} = 1.5 \text{ mol dm}^{-3}$; $\mu = 0.50 \text{ mol dm}^{-3}$; pH = 4.45

$[\text{NH}_2\text{CSNH}_2]/\text{mol dm}^{-3}$	$k_{\text{obs}}/\text{s}^{-1}$ 25°C	30°C	35°C	40°C	45°C
0.005	0.0611	0.0719	0.0810	0.0922	0.115
0.010	0.119	0.142	0.166	0.186	0.231
0.015	0.182	0.219	0.249	0.279	0.346
0.025	0.299	0.359	0.426	0.458	0.584
0.035	0.421	0.501	0.584	0.646	0.812
0.050	0.603	0.711	0.846	0.915	1.17
0.075	0.908	1.06	1.24	1.39	1.73
0.10	1.21	1.43	1.64	1.85	2.34
0.15	2.04	2.42	2.62	3.11	3.58
0.20	2.88	3.54	3.85	4.48	5.36
0.30	4.83	5.90	6.61	7.83	9.56
0.40	7.13	8.58	10.0	12.0	14.9
0.45	8.43	10.4	11.8	14.2	18.2
0.50	9.61	12.3	13.9	16.7	21.6
0.55	11.1	14.1	16.1	19.1	25.5
0.60	12.7	16.1	18.2	22.1	29.7

though the oxidant was always in excess. The ratio $\Delta[\text{Co(III)W}]^{5-}/\Delta[\text{NH}_2\text{CSNH}_2] = 1.0 \pm 0.03$ indicated that the stoichiometric equation of the reaction is expressible by eqn. (1).



Oxidation product

At the completion of the reaction between concentrated solutions of H_2NCSNH_2 and $[\text{Co(III)W}]^{5-}$, 200 mL of ethanol and 60 mL of concentrated HCl were added to the reaction mixture. It resulted in the formation of white crystals that were filtered, washed and dried in a vacuum desiccator. These crystals decomposed at 168 °C indicating that the crystals are those of formimidine dihydrochloride.²¹ The oxidation product of thiourea is formamidine disulfide²² and the dihydrochloride salt is formed in presence of concentrated hydrochloric acid.²² The other oxidation product was characterised to be $[\text{Co(II)W}]^{6-}$ by comparing the spectra of the spent reaction mixture with that of a solution prepared from its authentic sample.

Test for free radical

The reactant solutions, taken in separate glass stoppered conical flasks, were degassed with nitrogen before 1 mL of acrylonitrile was added to each solution. These clear solutions, no cloudiness was observed for some time, were mixed, swirled and left for sometime when cloudiness appeared indicating the formation of free radicals during the course of the reaction.

Mechanism and discussion

The order of the reaction with respect to thiourea is dependent on [thiourea] (Table 1). The reaction has strict first order dependence in $[\text{H}_2\text{NCSNH}_2] \leq 0.10 \text{ mol dm}^{-3}$ since the plot of k_{obs} against $[\text{H}_2\text{NCSNH}_2]$ passing through the origin indicated that no intermediates are involved and the bimolecular collision between $[\text{Co(III)W}]^{5-}$ and H_2NCSNH_2 molecules. The measurement of the optical density of reaction mixtures with increasing [thiourea] did not suggest the formation of any intermediate. At high [thiourea] $\geq 0.01 \text{ mol dm}^{-3}$ (Table 1), there are a simultaneous first and second-order paths since the plot of $k_{\text{obs}}/[\text{H}_2\text{NCSNH}_2]$ against $[\text{H}_2\text{NCSNH}_2]$ is linear indicating the formation of a weak intermediate C. A similar intermediate is suggested in the IrCl_6^{2-} oxidation,¹⁷ perhaps the only other study carried out under similar pH conditions, and that IrCl_6^{2-} is as substitution inert as $[\text{Co(III)W}]^{5-}$.

The results further indicate that the reactive thiourea species is very much dependent on the pH of the medium since $[\text{Co(III)W}]^{5-}$ ion is not affected by changes in pH¹ and $[\text{H}^+]$ ion.²

The rate is independent of pH (≤ 4.63) and then it increases at higher pH (≥ 4.63) (Table 2). This suggested the possibility of OH^- ion assisted dissociation of thiourea as considered in equilibrium (3). Similar equilibria have been considered in the oxidation of thiourea by IrCl_6^{2-} ion¹⁷ and in the oxidation of 1-octanethiol²³ by $\text{Fe}(\text{CN})_6^{3-}$ ion. The results are indicative of the higher reactivity of the anionic species compared to that of the molecular species.

The results in perchloric acid solutions (Table 3) indicated the possibilities of either the participation of H^+ in the rate-determining step or the participation of the mono-protonated thiourea as the reacting species. The first possibility is unlikely since the profile of the rate against $[\text{H}^+]$ is non-linear leaving the likely possibility of the protonated thiourea acting as the reactive species. The protonation of thiourea is known in solutions of strong acids,²⁴ and the protonated species is considered reactive in several redox reactions.^{7,8,9,25}

The rate–pH profile in the IrCl_6^{2-} oxidation of thiourea indicated monoprotated thiourea species are not formed¹⁷ at pH 1.1. Hence, in solutions of low pH (≤ 4.63) there is no other species present except H_2NCSNH_2 . This explains the observed independence of the rate on the ionic strength (Table 4) in buffer solution of pH 4.1. It is further concluded that the alkali metal ions are unlikely to mediate as a bridge between $[\text{Co(III)W}]^{5-}$ ion and the reactive thiourea species having no charge even though Li^+ ion-pairs with $[\text{Co(III)W}]^{5-}$ ion.

An attempt is made to propose a unified mechanism. The deduced rate law is then subjected to the prevailing experimental conditions under any given environment. The following reactions constitute the most plausible unified mechanism of the reaction.

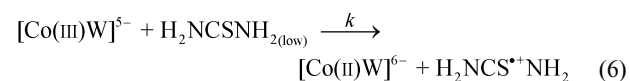
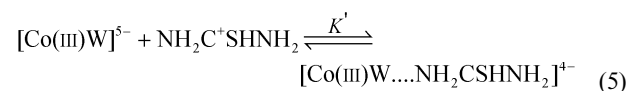
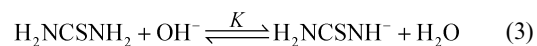
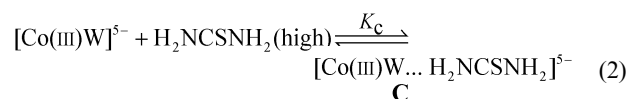


Table 2 The variation in k_{obs} values with pH at 49 °C. $10^4 [\text{Co(III)W}]^{5-} = 1.5 \text{ mol dm}^{-3}$; $[\text{NH}_2\text{CSNH}_2] = 0.15 \text{ mol dm}^{-3}$, $\mu = 0.50 \text{ mol dm}^{-3}$

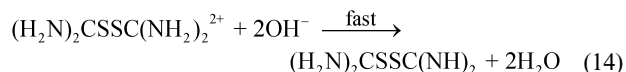
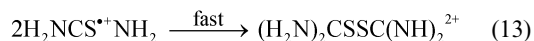
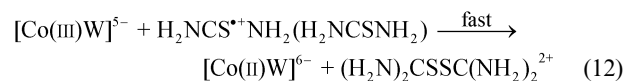
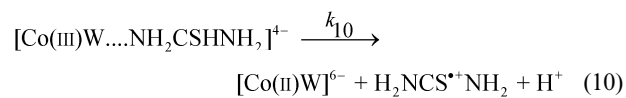
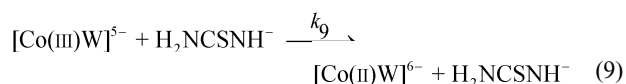
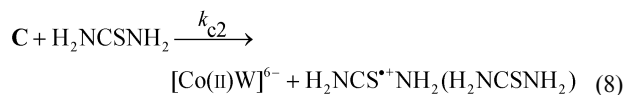
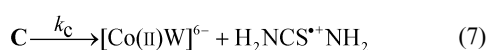
pH	3.40	3.60	3.95	4.23	4.45	4.63	4.80	4.99	5.23	5.57
$k_{\text{obs}}/\text{s}^{-1}$	4.03 ^a	4.01 ^a	4.05 ^a	4.01 ^a	4.03 ^a	4.01	4.17	4.27	4.79	5.95

^a Mean k_{obs} value = $4.03 \pm 0.02 \text{ s}^{-1}$.**Table 3** The dependence of k_{obs} on $[\text{H}^+]$ at constant ionic strength at 40 °C. $10^4 [\text{Co(III)W}]^{5-} = 1.5 \text{ mol dm}^{-3}$; $[\text{NH}_2\text{CSNH}_2] = 0.15 \text{ mol dm}^{-3}$; $\mu = 0.5 \text{ mol dm}^{-3}$

$[\text{H}^+]/\text{mol dm}^{-3}$	0.01	0.03	0.05	0.08	0.10	0.20	0.30	0.40	0.50
$k_{\text{obs}}/\text{s}^{-1}$	7.62	8.33	9.15	10.2	11.0	14.5	14.9	15.2	15.4

Table 4 The effect of ionic strength (μ) on the observed rate at 40 °C. $10^4 [\text{Co(III)W}]^{5-} = 1.5 \text{ mol dm}^{-3}$; $[\text{NH}_2\text{CSNH}_2] = 0.15 \text{ mol dm}^{-3}$; pH = 4.10^a

$\mu/\text{mol dm}^{-3}$	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45
$k_{\text{obs}}/\text{s}^{-1}$	3.13	3.10	3.12	3.15	3.21	3.22	3.14	3.12	3.08

^a Average $k_{\text{obs}} = 3.14 \pm 0.05 \text{ s}^{-1}$.

The rate law derived from the consideration of the above reactions is in eqn. (15)

The rate law (15) could be written as eqn. (16) considering that $K_a + [\text{H}^+] \gg KK_a[\text{OH}^-] + (k_cK_a + K'K_a^{-1}[\text{H}^+])[\text{H}_2\text{NCSNH}_2]$ where all the concentrations are the initial concentrations. The application of the rate law in eqn. (16) is discussed below under different experimental conditions.

Reaction in solutions pH ≤ 4.6 and low [thiourea]

The thiourea does not undergo any chemical change in solutions of pH ≤ 4.6 . Therefore, the reactive species is H_2NCSNH_2 . The reactions that contribute to the rate are the reactions (6) and (13). Thus, the rate law (16) accordingly changes to the eqn. (17).

$$\frac{-d[\text{Co(III)W}^{5-}]}{dt} = \frac{(k + k_cK_c + k_{c2}K_c[\text{H}_2\text{NCSNH}_2] + k_9K[\text{OH}^-] + k_{10}K'K_a^{-1}[\text{H}^+])[\text{Co(III)W}^{5-}][\text{H}_2\text{NCSNH}_2]}{K_a + [\text{H}^+] + KK_a[\text{OH}^-] + (k_cK_a + K'K_a^{-1}[\text{H}^+])[\text{H}_2\text{NCSNH}_2]} \quad (15)$$

$$k_{\text{obs}} = \frac{(k + k_cK_c + k_{c2}K_c[\text{H}_2\text{NCSNH}_2] + k_9K[\text{OH}^-] + k_{10}K'K_a^{-1}[\text{H}^+])[\text{H}_2\text{NCSNH}_2]}{K_a + [\text{H}^+]} \quad (16)$$

Table 5 The calculated values of k ($=k_{12}$), k_cK_c and $k_{c2}K_c$ ^a

Temp/°C	25	30	35	40	45
$k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	12.1	14.2	16.5	18.5	23.3
$k_cK_c/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	10.8	12.3	13.5	15.2	16.4
$k_{c2}K_c/\text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$	17.3	24.1	28.4	36.2	54.0

^a $\Delta H^{\ddagger}_k = 22.2 \pm 1.1 \text{ kJ mol}^{-1}$, $\Delta S^{\ddagger}_k = -150 \pm 3.6 \text{ J K}^{-1} \text{ mol}^{-1}$, $\Delta G^{\ddagger}_k = 66.9 \pm 0.9 \text{ kJ mol}^{-1}$, $\Delta H^{\ddagger}_{k_cK_c} = 14 \pm 1 \text{ kJ mol}^{-1}$, $\Delta S^{\ddagger}_{k_cK_c} = -161 \pm 2 \text{ J K}^{-1} \text{ mol}^{-1}$, $\Delta H^{\ddagger}_{k_{c2}K_c} = 40 \pm 4 \text{ kJ mol}^{-1}$, $\Delta S^{\ddagger}_{k_{c2}K_c} = -71 \pm 13 \text{ J K}^{-1} \text{ mol}^{-1}$.

$$k_{\text{obs}} = k[\text{H}_2\text{NCSNH}_2] \quad (17)$$

The values of k at different temperatures are in Table 5. The calculated values of the activation parameters are reported therein and would be discussed later.

Reaction in solutions \leq pH 4.6 and high [thiourea]

The simultaneous first and second-order dependence in $[\text{H}_2\text{NCSNH}_2]$ is explained by considering the reactions (2), (7), (8), (12) and (13). The rate law based on these reactions is given by the eqn. (18).

$$k_{\text{obs}} = (k_cK_c + k_{c2}K_c[\text{H}_2\text{NCSNH}_2])[\text{H}_2\text{NCSNH}_2] \quad (18)$$

The linear plots of $k_{\text{obs}}/[\text{H}_2\text{NCSNH}_2]$ against $[\text{H}_2\text{NCSNH}_2]$, Fig. 1, are consistent with the eqn. (18). The unflinching difference between the k and k_cK values ($k > k_cK$), Table 5, rationalises the reactions (2) and (7) as an alternative to the reaction (6) which occurs only at low $[\text{H}_2\text{NCSNH}_2]$ and in the absence of an intermediate. It is significant to note that the enthalpy of activation, ΔH^{\ddagger}_k , for the reaction at low $[\text{H}_2\text{NCSNH}_2]$ is 8 kJ mol^{-1} more than the $\Delta H^{\ddagger}_{k_cK_c}$ value at high $[\text{H}_2\text{NCSNH}_2]$. It is consistent with the fact that the enthalpy of activation for bimolecular collision path is higher than the path involving the decay of the intermediate for the formation of the intermediate is usually exothermic. The more negative value of the entropy, $\Delta S^{\ddagger}_{k_cK_c} = -161 \text{ J K}^{-1} \text{ mol}^{-1}$ is consistent with the relatively more ordered nature of the intermediate complex than the transition state formed in a reaction requiring the bimolecular collision. These observations thus rationalise the formation of the intermediate at high $[\text{H}_2\text{NCSNH}_2]$.

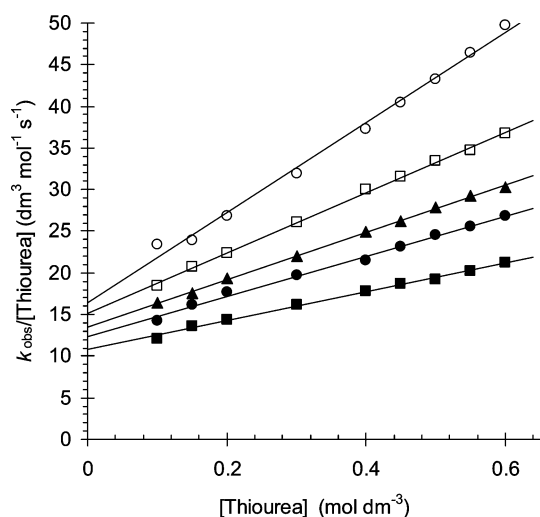
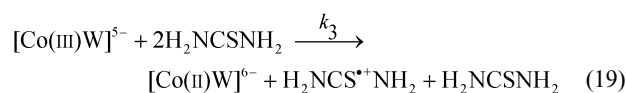


Fig. 1 The linear plots of $k_{\text{obs}}/[\text{H}_2\text{NCSNH}_2]$ against $[\text{H}_2\text{NCSNH}_2]$ with intercepts on the rate ordinate, consistent with the eqn. (18), at temperatures 25 (■), 30 (●), 35 (▲), 40 (□) and 45 °C (○). ($10^4[\text{Co(III)W}^{5-}]$ 1.5 mol dm⁻³, μ = 0.5 mol dm⁻³ and pH = 4.45).

The reaction (19), which could be an alternative to reaction (8), if the intermediate **C** is not assumed, is based on the highly improbable tri-molecular collision. This is one more reason for the assumption of the existence of the intermediate **C**, which is very likely in the presence of high concentrations of thiourea; **C** has been suggested to have a role in IrCl_6^{2-} oxidation.¹⁷



Reaction in buffer solutions \geq pH 4.6

The thiourea species present under the specified condition are H_2NCSNH_2 and H_2NCSNH^- that are in equilibrium through the reaction (3). The other reactions contributing to the rate are (2), (7), (9), (11), (13) and (14). The rate law (16) is therefore modified to the rate law in eqn. (20).

$$k_{\text{obs}} = (k_c K_c + k_9 K[\text{OH}^-])[\text{H}_2\text{NCSNH}_2] \quad (20)$$

If $[\text{OH}^-]$ is replaced by $K_w/[\text{H}^+]$, K_w is the ionization constant of water, the eqn. (20) is reduced to the final rate eqn. (21).

$$\frac{k_{\text{obs}}}{[\text{H}_2\text{NCSNH}_2]} = k_c K_c + \frac{k_9 K K_w}{[\text{H}^+]} \quad (21)$$

The required linear plot of $k_{\text{obs}}/[\text{H}_2\text{NCSNH}_2]$ against $[\text{H}^+]^{-1}$ ($[\text{H}^+] = 10^{-\text{pH}}$) with intercept, Fig. 2, is consistent with the eqn. (21). The values of the slope and intercept of the plot in Fig. 2 give $k_9 K K_w = 3.94 \times 10^{-5} \text{ s}^{-1}$ and $k_c K_c = 25.0 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively, at 49 °C. A value of $k_9 K = 7.18 \times 10^7 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ is obtained by substituting the K_w value, 5.47×10^{-13} at 50 °C.²⁶ Since the value of K is not known,¹⁷ therefore the value of k_9 could not be resolved. This supports the high reactivity of thiourea anion.

The reaction (22) could be an alternative to the reaction (9) if there is simultaneous second order dependence in $[\text{H}_2\text{NCSNH}_2]$. The inclusion of the reaction (22) in the mechanism would modify the rate law (21) to (23) without affecting the conclusion about the high reactivity of anionic thiourea species except that the numerical value of $k_9 K$ would be equal to $k_2 K_c K [\text{H}_2\text{NCSNH}_2]$.

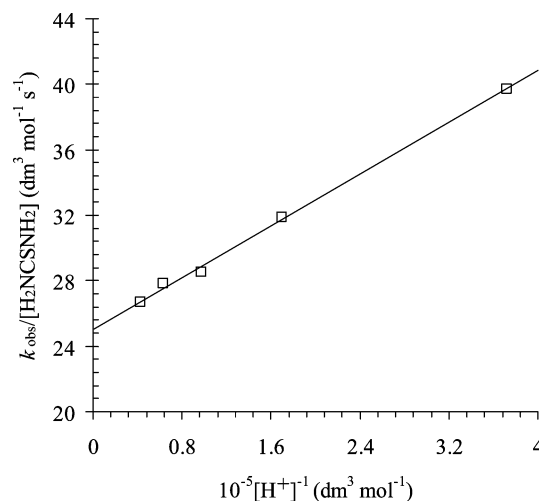
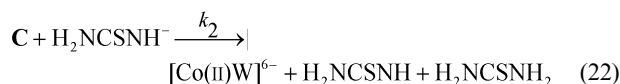


Fig. 2 The linear plot of $k_{\text{obs}}/[\text{H}_2\text{NCSNH}_2]$ against $[\text{H}^+]^{-1}$ with intercepts on the rate ordinate, consistent with the eqn. (21), in the pH range 4.63–5.7. The rate is independent of pH < 4.63. ($10^4[\text{Co(III)W}^{5-}]$ 1.5, $[\text{H}_2\text{NCSNH}_2]$ = 0.15 and μ = 0.5 mol dm⁻³, at 49 °C).

$$\frac{k_{\text{obs}}}{[\text{H}_2\text{NCSNH}_2]} = k_c K + \frac{k_2 K_c K K_w [\text{H}_2\text{NCSNH}_2]}{[\text{H}^+]} \quad (23)$$

Reaction in presence of strong acid

Since thiourea is known to be protonated in solutions of strong acids²⁴ and the protonated species is considered reactive in several redox reactions,^{7,8,9,25} the equilibria (2), (4), (5), reactions (7), (10) and (13) contribute to the rate under this condition. The rate law (16) is thus modified to the rate law in eqn. (24) which could be arranged to the eqn. (25).

$$k_{\text{obs}} = \frac{(k_{10} K' [\text{H}^+] + k_c K_c K_a) [\text{H}_2\text{NCSNH}_2]}{K_a + [\text{H}^+]} \quad (24)$$

$$\frac{k_{\text{obs}} (K_a + [\text{H}^+])}{[\text{H}_2\text{NCSNH}_2]} = (k_{10} K' [\text{H}^+] + k_c K_c K_a) \quad (25)$$

The linear plot of the left hand side of eqn. (25) against $[\text{H}^+]$, with $K_a = 0.066 \text{ mol dm}^{-3}$ at 25 °C (ref. 23) since the value at 40 °C is not known, is in Fig. 3. The use of $K_a = 0.048 \text{ mol dm}^{-3}$, selected by the method of trial and error based on the criterion that the plot should not show any curvature, also resulted in a linear plot with the intercept = 0.744 s^{-1} and slope = $116 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Thus $k_c K_c = 15.5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ is obtained at 40 °C, which is in close agreement with the value of $15.2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ obtained from the data under excess of thiourea and $\text{pH} \leq 4.6$. This close agreement between the $k_c K_c$ values from the two data under different conditions is a strong support for the commonality of the reactions (2) and (7) under two different conditions and the correctness of the K_a value at 40 °C. The other plots in Fig 3 are for the other arbitrary values of $K_a = 0.03$ that show positive curvature (yielding a negative intercept suggesting that the chosen K_a value is unacceptable) and 0.2 that shows a negative curvature (yielding a positive intercept with a higher intercept value). The value of $k_{10} K' = 116 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ rationalises the high reactivity of the protonated thiourea species.

Reactive form of protonated thiourea

The two tautomeric forms **A** and **B** of protonated thiourea are known to exist in acidic solution.²⁴ The observed rate, therefore, refers to the reaction either with any one of the tautomeric form or both. It is difficult to characterize the reactive tautomeric species based on the present rate data.

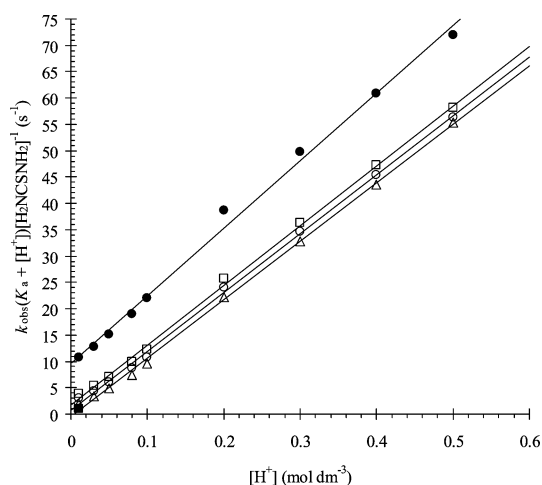
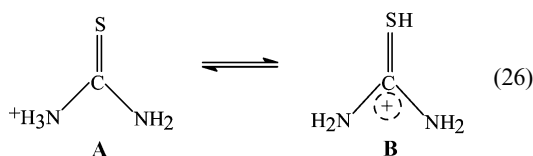


Fig. 3 The linear plots of $k_{\text{obs}}(K_a + [\text{H}^+])/[\text{H}_2\text{NCSNH}_2]$ against $[\text{H}^+]$ for K_a values, chosen arbitrarily, = 0.03 (Δ), 0.2 (\bullet), lit.,²³ = 0.066 (\square) and the chosen value at 40 °C = 0.048 mol dm⁻³ (\circ). ($10^4[\text{Co(III)W}^{5-}]$ 1.5, $[\text{H}_2\text{NCSNH}_2]$ = 0.15 mol dm⁻³ and μ = 0.5 mol dm⁻³).



However, a guess about the reactive tautomer is attempted by comparing the kinetics of the present oxidation with those of hydroxylamine,² hydrazine³ and azide⁴ which are protonated at the NH_2 group in acidic solutions. Since a retardation in the observed rate with increasing H^+ ion is not realized,^{2,4} the seat of the reaction can not be at NH_2 group. Therefore the likely seat of reaction is the S atom in the enol form that explains the different kinetic behaviour of thiolactic acid,¹ the seat of the reaction being the protonated S atom, from thiourea. The common reason for the retardation of the rate in thiolactic acid,¹ hydroxylamine,² hydrazine³ and azide,⁴ is the non-availability of the electron pair at the seat of the reaction. It is for this reason that the reactive protonated thiourea is represented as $\text{NH}_2\text{C}^+\text{SHNH}_2$ where the positive charge is spread over the C atom as shown in the structure **B** of the two tautomeric forms.

Marcus cross relation

The Marcus theory⁶ can be used to estimate the self-exchange rate of the unknown $2\text{H}_2\text{NCSNH}_2-(\text{H}_2\text{N})_2\text{CSSC}(\text{NH}_2)_2$ couple by adopting a method based on the free energies²⁷ as described in the following equations. In eqn. (27), ΔG_{12}° is the free energy of activation for a cross reaction, ΔG_{11}° and ΔG_{22}° are the free energies of activation for the self-exchange reactions of oxidant and reductant couples; Δw , the electric work term required to bring the reactants i and j to the contact distance σ ($= r_i + r_j$) in the precursor complex, is given by the eqn. (28) and the free energy change for the cross reaction, ΔG_{12}° , is given by the eqn. (29). In eqn. (30), N_A is the Avogadro number, z_i and z_j are the charges on the reactants, ϵ and ϵ_0 are the permittivity of the bulk medium and in vacuum respectively and κ is defined in eqn. (31). Similarly, k_B and h are the Boltzmann and Planck constants respectively in the Eyring equation, eqn. (32), which is used to determine the free energies of activation.

$$\Delta G_{12}^{\circ} = 0.5(\Delta G_{11}^{\circ} + \Delta G_{22}^{\circ} + \Delta G_{12}^{\circ} + \Delta w) \quad (27)$$

$$\Delta w = w_{12} + w_{21} - w_{11} - w_{22} \quad (28)$$

$$\Delta G_{12}^{\circ} = -nFAE^{\circ} \quad (29)$$

$$w_{ij} = z_i z_j e_0^2 N_A / 4\pi\epsilon\epsilon_0\sigma(1 + \kappa\sigma) \quad (30)$$

$$\kappa = (2e_0^2 N_A \mu / \epsilon\epsilon_0 k_B T)^{1/2} \quad (31)$$

$$k_{ij} = k_B T h^{-1} \exp(-\Delta G_{ij}^{\circ} / RT) \quad (32)$$

The ΔG_{12}° , calculated with E_{22}° ($2\text{H}_2\text{NCSNH}_2 + 2e^- \rightleftharpoons (\text{H}_2\text{N})_2\text{CSSC}(\text{NH}_2)_2$) = 0.418 V,²⁸ and E_{11}° = 1.01 V,²⁹ is -114.2 kJ mol⁻¹. The ΔG_{11}° , calculated with k_{11} = 0.91 dm³ mol⁻¹ s⁻¹ at μ = 0.5 mol dm⁻³ and 25 °C,³⁰ is 73.2 kJ mol⁻¹. The electric work terms, w_{11} = 16, w_{21} = -9.69 , w_{12} = w_{22} = 0 kJ mol⁻¹ were calculated from eqn. (30) using r_{11} = 0.5 nm and r_{22} = 0.28 nm, calculated from the relation $r = \sqrt[3]{(3 \times \text{Mol. Wt.} / 4\pi \times N_A \times \text{density})}$.³¹ The value of κ , obtained with eqn. (31), is 2.32×10^9 nm⁻¹. The ΔG_{22}° , from substituting the known values of Δw , ΔG_{11}° , ΔG_{12}° (66.9 kJ mol⁻¹, Table 5) and ΔG_{12}° in eqn. (27), is 200.4 kJ mol⁻¹ which gives an extremely low value of k_{22} , 4.86×10^{-23} dm³ mol⁻¹ s⁻¹. The extremely low value is possibly due to S-S bonds in the dimeric $(\text{H}_2\text{N})_2\text{CSSC}(\text{NH}_2)_2$ species. The simple Marcus theory, given by eqn. (33), is valid when the driving force is not too large, $\ln f_{12} \approx 0$ and the work terms cancel (see eqn. (36)), has been used with considerable success.

$$k_{12} = (k_{11} k_{22} K_{12})^{0.5} \quad (33)$$

The predicted rate (value of k_{12}), calculated from the eqn. (33), using the estimated value of k_{22} is about 2700 times slower than the observed rate indicating the breakdown of the Marcus theory. The breakdown of the Marcus theory has been reported in the Ce(IV) sulfate oxidation of thiourea probably due to the strong interaction between the reactants involved in the formation of the free radicals.⁷ The reactions of *N*-alkylphenothiazines with $\text{Fe}_{\text{aq}}^{3+}$ ion³² and $\text{Mn}_{\text{aq}}^{3+}$ ion³³ are 300–500 times slower than the predicted one.

One of the referees pointed out that the calculated value of the self-exchange rate constant k_{22} , using the eqn. (34) and (35), is 7×10^{-16} dm³ mol⁻¹ s⁻¹ which is at least six orders of magnitude more positive than the value obtained from the consideration of the free energies.

$$k_{12} = (k_{11} k_{22} K_{12} \log f_{12})^{0.5} \quad (34)$$

where $\log f_{12}$ is expressed by the eqn. (35).

$$\log(\log f_{12}) = (\log K_{12})^2 / 4 \log(k_{11} k_{22} / Z^2) \quad (Z^2 = 10^{22}) \quad (35)$$

If one puts the experimental values for k_{11} , k_{12} , K_{12} and $\log f_{12}$ = 2.1×10^{-3} (obtained by back calculation) into eqn. (34) one obtains a value of 7×10^{-16} dm³ mol⁻¹ s⁻¹ for k_{22} . However, if the values of k_{11} , K_{12} and k_{22} (4.86×10^{-23} dm³ mol⁻¹ s⁻¹) are substituted then the calculated value of k_{12} is 3.2×10^{-2} dm³ mol⁻¹ s⁻¹ which is much less than the experimental value of 12.1 dm³ mol⁻¹ s⁻¹.

The breakdown of the eqn. (33) suggested that the driving force is probably large, the f_{12} term may be significant and the work terms are not cancelling and therefore there is necessity to consider the use of the modified expression³⁴ given in eqn. (36).

$$k_{12} = (k_{11} k_{22} K_{12} f_{12})^{0.5} W_{12} \quad (36)$$

where

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21}) / RT]^2}{4[\ln(k_{11} k_{22} / A_{11} A_{22}) + (w_{11} + w_{22}) / RT]} \quad (37)$$

$$W_{12} = \exp\left[-\frac{(w_{12} + w_{21} - w_{11} - w_{22})}{2RT}\right] \quad (38)$$

The eqn. (37) and (38) were solved using a computer program. The estimate of k_{22} was obtained from an iterative

Table 6 The values of k_{12} ($=k_{\text{obs}}/[\text{substrate}]$) and ΔE° for some nitro-genous compounds¹⁸

Substrate	Hydrazine	GSH ^a	HNO ₂	Thiourea
k_{12}	0.018	5×10^7	1.22	12.5×10^3
ΔE°	-0.27	0.78	0.07	0.59

^a GSH = reduced glutathione.

procedure. Initially a guessed value of k_{22} was supplied to the program which returned the values of k_{22} and f_{12} ; the value of k_{22} so obtained was used next when fresh values of k_{22} and f_{12} were returned by the program. The procedure was repeated till constant values of k_{22} and f_{12} were obtained. The final values obtained were: $k_{22} = 2.44 \times 10^{-10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $f_{12} = 0.168$. The values of K_{12} and W_{12} were 8.74×10^8 and 67 respectively and remained constant throughout.

Thus, the value of k_{22} obtained from the use of the modified eqn. (36)–(38) is at least five orders of magnitude more positive than the value obtained from the use of eqn. (34) and (35). This signifies the importance of the work terms.

It is of interest to re-plot the data of the previous authors, (Table 6),¹⁸ who plotted $\log k_{12}$ against E° and obtained a linear plot with a slope value -8.6 , by correctly plotting $\log k_{12}$ against ΔE° (the difference of the redox potentials of the oxidant and reductant). The eqn. (33) could be written as eqn. (39) where K_{12} is related to ΔE° by the eqn. (40) with n denoting the total number of electrons changing in the reaction. The $n = 1$ was assumed by the previous authors.¹⁸ The substitution of $\log K_{12}$ in eqn. (39) by $\Delta E^\circ/0.0591$ gives the eqn. (41) which suggests a linear plot when $\log k_{12}$ is plotted against ΔE° with a slope equal to 8.46.

$$\log k_{12} = 0.5(\log k_{11} + \log k_{22} + \log f) + 0.5 \log K_{12} \quad (39)$$

$$\log K_{12} = n\Delta E^\circ/0.0591 \quad (40)$$

$$\log k_{12} = 0.5(\log k_{11} + \log k_{22} + \log f) + 8.46\Delta E^\circ \quad (41)$$

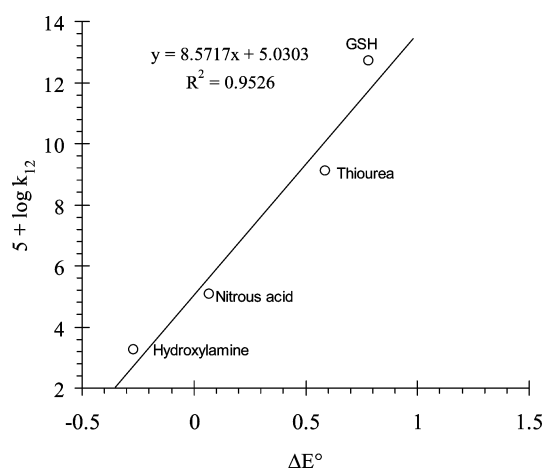


Fig. 4 The linear plot of $\log k_{12}$ ($=k_{\text{obs}}/[\text{H}_2\text{NCSNH}_2]$) against ΔE° has a slope of 8.6 against the expected value of 8.5.

The required plot, Fig. 4, is linear with a slope value 8.6 which is in fair agreement with the predicted slope value of 8.5, corroborates the outer-sphere nature of the reaction.

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References

- Raj N. Mehrotra, S. Dholiya, Kamla Sharma and A. Prakash, *Indian J. Chem., Sect. A*, 1998, **37**, 973.
- B. Goyal, A. Prakash and Raj N. Mehrotra, *Indian J. Chem.*, 1999, **38A**, 541.
- Rupa Shah, A. Prakash and Raj N. Mehrotra, *Indian J. Chem.*, 1999, **38A**, 680.
- B. Goyal, Manu Mehrotra, A. Prakash and Raj N. Mehrotra, *Inorg. React. Mech.*, 2000, **1**, 289.
- J. Burgess, *Ions in Solutions*, Ellis Horwood, Chichester, 1988.
- R. A. Marcus, *J. Phys. Chem.*, 1963, **67**, 853; R. A. Marcus, *J. Phys. Chem.*, 1968, **72**, 891; R. A. Marcus, *Annu. Rev. Phys. Chem.*, 1964, **15**, 155.
- U. D. Gomwalk and A. McAuley, *J. Chem. Soc. A*, 1968, 2948.
- A. McAuley and U. D. Gomwalk, *J. Chem. Soc. A*, 1969, 977; A. McAuley and R. Shanker, *J. Chem. Soc., Dalton Trans.*, 1973, 2321.
- G. Davies, *Inorg. Chem.*, 1972, **11**, 2488.
- G. Davies and D. J. Loose, *Inorg. Chem.*, 1976, **15**, 694; G. Davies, R. Higgins and D. J. Loose, *Inorg. Chem.*, 1976, **15**, 700.
- M. Hoffmann and J. O. Edwards, *Inorg. Chem.*, 1977, **16**, 3333.
- G. Rabi and M. T. Beck, *J. Chem. Soc., Dalton Trans.*, 1985, 1669.
- Z. Amjad and A. McAuley, *Inorg. Chim. Acta*, 1977, **26**, 127.
- M. Putselnik and R. Sokoniewicz, *Monatsh. Chem.*, 1978, **109**, 33.
- J. D. Lydon and R. C. Thompson, *Inorg. Chem.*, 1984, **23**, 3694.
- S. Gangopadhyay, S. K. Saha and P. Banerjee, *Transition Met. Chem.*, 1991, **16**, 355.
- H. N. Po, H. Eran, Y. Kim and J. E. Byrd, *Inorg. Chem.*, 1979, **18**, 197.
- M. A. Olataunji, G. A. Ayoko and F. O. Ohiani, *Transition Met. Chem.*, 1994, **19**, 253.
- L. C. W. Baker and T. P. McCutcheon, *J. Am. Chem. Soc.*, 1956, **78**, 4503.
- Vogel's Textbook of Quantitative Inorganic Analysis*, 4th edn., Longman, 1986, p. 45.
- P. W. Priestler and L. Berger, *J. Am. Chem. Soc.*, 1947, **69**, 232.
- P. W. Priestler, *J. Am. Chem. Soc.*, 1949, **71**, 2849.
- K. B. Wiberg, H. Maltz and M. Okano, *Inorg. Chem.*, 1968, **7**, 830.
- T. J. Lane, J. A. Ryan and L. J. Walter, *J. Am. Chem. Soc.*, 1956, **78**, 5560.
- W. A. Alexander, C. J. Mash and A. McAuley, *Analyst (London)*, 1970, **95**, 675.
- Handbook of Chemistry and Physics*, ed. C. D. Hodgman, The Chemical Rubber Publishing Co., Boca Raton, FL, 1962, p. 1752.
- A. Wanat, R. van Eldik and G. Stochel, *J. Chem. Soc., Dalton Trans.*, 1998, 2497.
- P. W. Priselser and L. Berger, *J. Am. Chem. Soc.*, 1947, **69**, 322.
- L. Ebersson, *J. Am. Chem. Soc.*, 1983, **105**, 3192.
- P. Rasmussen and C. H. Brubaker, Jr., *Inorg. Chem.*, 1964, **3**, 977.
- M. E. Peover, *Electrochim. Acta*, 1968, **13**, 1083; H. Kojima and A. J. Bard, *J. Am. Chem. Soc.*, 1975, **97**, 6317.
- E. Pelizzetti and E. Mentasti, *Inorg. Chem.*, 1979, **18**, 583.
- E. Pelizzetti, *J. Chem. Soc., Dalton Trans.*, 1980, 484.
- D. H. Macartney and N. Sutin, *Inorg. Chem.*, 1983, **22**, 3530 and ref. 36(a).