Kinetics and Mechanisms of the Reaction between Thioacetamide and Lead(II), Cadmium(II), and Cobalt(II) Ions in Acetate Buffered Solution

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The interaction between thioacetamide and lead(II), cadmium(II), and cobalt(II) ions in acetate buffered solution leads to acetonitrile and metal sulphide. A mechanism is suggested which involves the rate-determining decomposition of the deprotonated form of 1 : 1 metal–thioacetamide complexes. The mechanism accounts for the rate dependence on thioacetamide, hydrogen ion, and metal ion concentration. The influence of the nature of the metal ions on the reaction rate, characterised by the sequence Pb > Cd > Co, is discussed in the light of the hard–soft acid–base principle. The difference in mechanism between the hydrogen ion and metal ion catalysed reaction of thioacetamide is also rationalised.

THIOACETAMIDE (TAA) is used as an alternative to hydrogen sulphide for the precipitation of metal ions in qualitative and quantitative analysis. Several kinetic studies [1-8] have shown that the precipitation of metal sulphides by TAA can occur by two distinct reaction paths, depending upon the circumstances. At pH < 3 it is usually found that TAA is first hydrolysed to hydrogen sulphide, whereupon metal sulphide precipitates. At pH > 3 a direct interaction between metal ion and TAA leads to the metal sulphide.

In most previous work the precipitation rate of the metal sulphide was indirectly determined from the concentration of the metal ion remaining in solution after timed intervals. In none of these studies has a plausible reaction mechanism been formulated.

In the present study the disappearance of TAA has been measured directly. This allowed us to examine the kinetic effect of the metal ion on the hydrolysis rate of TAA. The reactions were studied in the pH range 5—6 at 80 °C where they occurred at a measurable rate. The use of a pH stat method, as was done in our previous studies of the hydrolysis of TAA,[9,10] was impossible because of local metal hydroxide precipitation. Therefore an acetate buffer was selected to keep the pH constant.

EXPERIMENTAL

Reagents.—All reagents were AnalaR grade. The stock solutions were prepared by weight without further purification. They were: 0.012 5M-TAA; 0.1M-$Pb(ClO_4)_2$; 1M-$CdCl_2$; 1M-$CoCl_2$; 1M-NaOAc; and 1M-$NaClO_4$. A 2.5M-acetic acid solution was used to adjust the pH to the desired value. The glass electrode was calibrated with a 0.05M-potassium hydrogen phthalate solution. Other solutions were 0.05M-EDTA and 0.05M-zinc acetate.

Apparatus.—The reaction vessel with the accessories was the same as that used previously.[9,10] The measurement of the absorbance of TAA at 261.5 nm was performed continually by circulating the reaction solution by means of a peristaltic pump (L. K. B. Varioperpex). The solution was successively pumped through a sintered glass filter of porosity 2, a spiral glass tube immersed in a thermostatted bath at 20 °C, and a flow-through cell. The transmission of the solution was registered on a Tacussel Graphispot recorder from which the absorbance at each moment was calculated.

Procedure.—An aqueous solution (250 ml) containing known concentrations of sodium acetate and sodium perchlorate was thermostatted in the reaction vessel. The pH was adjusted to 6.5 with the pH stat mode of the autotitrator. The stock or diluted solution (25 ml) of the metal ion was added, except in experiments to study the effect of buffer components; the pH was adjusted to the predetermined value. The peristaltic pump was started and the transmission set to 100%. 0.012 5M-TAA solution (1 ml) was added, the recorder started, and the change in transmission followed as a function of time.

At the end of the experiment, after centrifugation and filtration of the precipitate formed, the metal ion concentration was determined titrimetrically with EDTA at pH 5 and 70 °C, using Xylenol Orange as indicator.

RESULTS AND DISCUSSION

Effect of Buffer Components on the Hydrolysis Rate of TAA.—The increase of the hydrolysis rate of TAA in ammonia and carbonate buffers [11] shows that ignoring the effects of the buffer components may lead to unexpected results. It was therefore necessary to study the influence of the acetate buffer employed. The observed rate constants at different buffer concentrations and pH are given in Table 1.

In the presence of an acetate buffer the observed rate constant can be written as (1). By expressing [HOAc]

$$k_{\mathrm{obs.}} = k_0 + k_{\mathrm{H_3O^+}}a_{\mathrm{H_3O^+}} + k_{\mathrm{OH^-}}a_{\mathrm{OH^-}} + k_{\mathrm{HOAc}}[\mathrm{HOAc}]f_{\mathrm{HOAc}} + k_{\mathrm{OAc^-}}[\mathrm{OAc^-}]f_{\mathrm{OAc^-}} \qquad (1)$$

as a function of [OAc^-] equation (1) becomes (2). A plot

$$k_{\mathrm{obs.}} = k_0 + k_{\mathrm{H_3O^+}}a_{\mathrm{H_3O^+}} + k_{\mathrm{OH^-}}a_{\mathrm{OH^-}} + \left(k_{\mathrm{OAc^-}} + \frac{k_{\mathrm{HOAc}}a_{\mathrm{H_3O^+}}}{K_\mathrm{a}}\right)[\mathrm{OAc^-}]f_{\mathrm{OAc^-}} \qquad (2)$$

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of the rate constants, at two different pH values, as a function of OAc^- concentration gives straight lines. At pH 5.50 the slope and intercept obtained were 2.26×10^{-4} (standard deviation s 0.311×10^{-4}) and 8.10×10^{-5} (s 0.85×10^{-5}); at pH 6.00 2.37×10^{-4} (s 0.24×10^{-4}) and 8.15×10^{-5} (s 0.65×10^{-5}), respectively. From these results, and the known rate constants of the hydrogen ion[9] and hydroxide ion[10] catalysed hydrolyses, the rate constant of the spontaneous reaction with water, k_0, and the catalytic constants k_{HOAc} and k_{OAc^-} were calculated. The activity coefficient f_{OAc^-} was ignored. The constants obtained were: k_0 8.0×10^{-5} min^{-1}, k_{HOAc} 6.71×10^{-5}, and k_{OAc^-} 2.21×10^{-4} l mol^{-1} min^{-1}. Since the difference between the slopes of the straight lines is smaller than the standard deviations the value of k_{HOAc} is not significant. The values of k_0 and k_{OAc^-} reveal that the spontaneous reaction is very slow and that OAc^- has a positive catalytic effect. The latter probably results from a general base catalysis although a nucleophilic reaction is also possible.

TABLE 1

Effect of buffer concentration on the first-order rate constant of TAA hydrolysis at 80 °C and I 0.4

$[OAc^-]$/M	pH 5.50 $10^4k_{obs.}/min^{-1}$	pH 6.00 $10^4k_{obs.}/min^{-1}$
0.1	1.09	1.08
0.2	1.25	1.18
0.3	1.49	1.52
0.4	1.80	1.72

To obtain a constant catalytic effect by the acetate species a 0.09M-OAc^- concentration was used in all subsequent work.

The Metal–Thioacetamide Interaction.—Products. Experiments similar to the kinetic runs, except that the TAA concentration was 0.01M instead of 5×10^{-5}M, were performed to identify the products of the metal–TAA interaction. Analysis by g.l.c. on a Porapak Q column showed that the organic reaction product was acetonitrile. Quantitative experiments with an internal standard (CH_3OH) gave acetonitrile concentrations which agree within 10—20% with the amounts of TAA used up. The precipitated inorganic products were identified, after filtration and drying, by X-ray powder diffraction as PbS, CdS, and β-CoS.

Kinetics. Plots of the logarithm of the absorbance, due to the TAA concentration, as a function of reaction time are linear over more than one half-live. The disappearance of TAA is consequently a first-order reaction. The values of k_{obs} are reproducible to within 3%.

(a) Effect of metal ion concentration. The observed rate constants at pH 6 and at different initial metal ion concentrations are given in Table 2. The order with respect to the initial metal ion concentration was obtained by linear regression and amounts to 0.84 (s 0.058) for the Pb–TAA, 0.84 (s 0.031) for the Cd–TAA, and 1.14 (s 0.088) for the Co–TAA interaction.

(b) Effect of pH. The rate constants obtained at different pH and at constant metal ion concentration are summarized in Table 2. The order with respect to the hydrogen ion activity is −1.02 (s 0.047) for the Pb–TAA, −1.05 (s 0.042) for the Cd–TAA, and −1.07 (s 0.039) for the Co–TAA interaction. The reaction is consequently inversely first order with respect to hydrogen ion activity.

TABLE 2

Effect of the metal ion concentration and pH on the reaction rate of the Pb–TAA, Cd–TAA, and Co–TAA interaction at 80 °C and I 0.36

System	$10^2[M^{2+}]$/M	$10^3k_{obs.}/min^{-1}$ pH 6.00	pH	$10^3k_{obs.}/min^{-1}$ $[Cd^{2+}] = [Co^{2+}] = 10[Pb^{2+}] = 0.09$M
Pb–TAA	0.896	12.0	5.00	1.23
	0.717	9.2	5.25	1.82
	0.538	8.58	5.50	3.68
	0.358	5.6	5.75	6.87
	0.179	3.02	6.00	12.0
Cd–TAA	9.08	26.2	5.00	2.26
	7.21	20.7		
	5.32	16.4	5.50	7.1
	3.59	11.2	5.75	12.5
	1.82	6.8	6.00	26.2
Co–TAA	8.95	8.3	5.00	0.729
	7.22	6.4	5.25	1.41
	5.51	4.9	5.50	2.51
	3.48	3.4	5.75	5.27
	1.86	1.3	6.00	8.3

(c) Effect of ionic strength. A change of the ionic strength from 0.36 to 0.14 revealed no particular effect on the reaction rate.

(d) Effect of temperature. The reactions were carried out in the temperature range 60—90° and the results are collected in Table 3. The activation energies were obtained from a plot of log k_{obs} against T^{-1}. They are 21.5 (s 0.33) for the Pb–TAA, 23 (s 1.5) for the Cd–TAA, and 24.1 kcal mol^{-1} (s 0.31 kcal mol^{-1}) for the Co–TAA interaction.

TABLE 3

Effect of temperature on the reaction rate of the Pb–TAA, Cd–TAA, and Co–TAA interaction at pH 6.00, I 0.36 and $[Cd^{2+}] = [Co^{2+}] = 10[Pb^{2+}] = 0.09$M

t/°C	Pb–TAA $10^3k_{obs.}/min^{-1}$	Cd–TAA $10^3k_{obs.}/min^{-1}$	Co–TAA $10^3k_{obs.}/min^{-1}$
60	1.98	3.7	1.04
70	5.14	8.0	2.9
80	12.0	26.2	8.3
90	29.7	60	20.8

Mechanism. The experimental results show that the reaction rate is defined by the concentrations of TAA, metal ion, and hydronium ion. The rate contribution for loss of TAA *via* OAc^- catalysed hydrolysis is small compared with the observed rate so that it can be ignored.

The reaction products identified are acetonitrile and metal sulphide. The overall reaction scheme compatible with these results is given by equation (3).

$$CH_3CSNH_2 + M^{2+} + 2\,H_2O \longrightarrow CH_3CN + MS + 2H_3O^+ \quad (3)$$

In order to understand the observed reaction orders and the effect of ionic strength a multiple step reaction mechanism has to be considered (Scheme). The proper rate-determining steps (12)—(14) are preceded by a number of fast equilibria (4)—(11). In all reactions solvating water molecules were omitted for simplicity. Equilibria like (15) are ignored because under the given

$$[\mathrm{M(H_2O)}_n]^{2+} + \mathrm{H_2O} \rightleftharpoons [\mathrm{M(H_2O)}_{n-1}\,\mathrm{OH}]^{+} + \mathrm{H_3O^+} \qquad (15)$$

circumstances the concentration of hydroxo-complexes is $<1\%$ of the initial metal ion concentration. On the other hand monochloro [reaction (4)] and monoacetato [reaction (5)] complexes are formed in a significant proportion ($>50\%$).[12]

$$\mathrm{M^{2+} + Cl^- \overset{K_1}{\rightleftharpoons} MCl^+} \qquad (4)$$

$$\mathrm{M^{2+} + OAc^- \overset{K_2}{\rightleftharpoons} MOAc^+} \qquad (5)$$

$$\mathrm{M^{2+} + TAA \overset{K_3}{\rightleftharpoons} \underset{(I)}{MTAA^{2+}}} \qquad (6)$$

$$\mathrm{MCl^+ + TAA \overset{K_4}{\rightleftharpoons} \underset{(II)}{MClTAA^{+}}} \qquad (7)$$

$$\mathrm{MOAc^+ + TAA \overset{K_5}{\rightleftharpoons} \underset{(III)}{MOAcTAA^{+}}} \qquad (8)$$

$$\mathrm{MTAA^{2+} + H_2O \overset{K_6}{\rightleftharpoons} \underset{(IV)}{MTAA^{+}} + H_3O^+} \qquad (9)$$

$$\mathrm{MClTAA^{+} + H_2O \overset{K_7}{\rightleftharpoons} \underset{(V)}{MClTAA} + H_3O^+} \qquad (10)$$

$$\mathrm{MOAcTAA^{+} + H_2O \overset{K_8}{\rightleftharpoons} \underset{(VI)}{MOAcTAA} + H_3O^+} \qquad (11)$$

$$\mathrm{MTAA^{+} + H_2O \xrightarrow{k_9} MS + CH_3CN + H_3O^+} \qquad (12)$$

$$\mathrm{MClTAA + H_2O \xrightarrow{k_{10}} MS + CH_3CN + H_3O^+ + Cl^-} \qquad (13)$$

$$\mathrm{MOAcTAA + H_2O \xrightarrow{k_{11}} MS + CH_3CN + H_3O^+ + OAc^-} \qquad (14)$$

SCHEME Reaction mechanism of the metal thioacetamide interaction. [In the Pb–TAA reaction equations (4), (7), (10), and (13) have not to be considered, due to the absence of $\mathrm{Cl^-}$ ions]

Although in this study no spectrophotometric evidence was found for the rapid formation of detectable quantities of metal–TAA complexes [reactions (6)—(8)], they have been prepared under well defined conditions. From *X*-ray diffraction data on single crystals could be concluded that the metal is co-ordinatively bound to the sulphur atom.[13-15] Reactions (9)—(11) follow from the fact that in thioamides co-ordination through the sulphur atom always decreases the CS stretching frequency and generally increases the CN stretching frequency of the free ligand.[16-18] These shifts indicate that mesomeric structure B is favoured, permitting an easier release of an amino-proton.

$$\underset{\textstyle\mathrm{A}}{\mathrm{CH_3C(NH_2){:}S \rightarrow M}} \longleftrightarrow \underset{\textstyle\mathrm{B}}{\mathrm{CH_3C({:}NH_2)S{-}M}}$$

The proposed mechanism leads to the rate equation (16) which is compatible with the orders observed for

$$\begin{aligned}-\mathrm{d[TAA]/d}t &= k_9[\mathrm{(IV)}] + k_{10}[\mathrm{(V)}] + k_{11}[\mathrm{(VI)}] \\ &= k_9K_6\frac{[\mathrm{(I)}][\mathrm{H_2O}]}{[\mathrm{H_3O^+}]} + k_{10}K_7\frac{[\mathrm{(II)}][\mathrm{H_2O}]}{[\mathrm{H_3O^+}]} + k_{11}K_8\frac{[\mathrm{(III)}][\mathrm{H_2O}]}{[\mathrm{H_3O^+}]} \\ &= (k'_9K_6K_3[\mathrm{M^{2+}}] + k_{10}'K_7K_4[\mathrm{MCl^+}] + k_{11}'K_8K_5[\mathrm{MOAc^+}])\frac{[\mathrm{TAA}]}{[\mathrm{H_3O^+}]} \qquad (16)\end{aligned}$$

$$\therefore k_{\mathrm{obs}} = \frac{1}{[\mathrm{H_3O^+}]}(k_9'K_6K_3[\mathrm{M^{2+}}] + k_{10}'K_7K_4[\mathrm{MCl^+}] + k_{11}'K_8K_5[\mathrm{MOAc^+}]) \qquad (17)$$

TAA and $\mathrm{H_3O^+}$. It also accounts for the obtained fractional order with respect to the initial metal ion concentration since (i) it may be expected that the metal ion complexes involved will react with TAA at a different rate and (ii) the concentration ratios of these complexes depend on the initial metal ion concentration.

The proposed slow steps (12)—(14) are bimolecular reactions involving at least one neutral molecule. The rate of such steps would not be expected to be very susceptible to changes in ionic strength. Although variation of the ionic strength has some effect on the equilibria preceding the rate-determining steps, this effect will be small, in the region 0.1—0.4 *I*, as can be calculated using activity coefficients obtained by the Davies equation.[19]

To discuss the rate differences between the metal–TAA interactions, Pearson's hard–soft acid–base (HSAB) principle [20] can be applied. Due to the delocalisation of the π system in the thioamide function, TAA is a soft base with sulphur softer than nitrogen. Consequently, borderline and soft acids will co-ordinate through sulphur, as confirmed in the crystallized complexes.[13-15] The metal–sulphur bond strength is expected to decrease from Cd through Pb to Co. Measurements on the stability constants of Cd and Pb thiourea complexes,[12] a ligand which is isoelectronic with TAA, show this order.

In the present study, however, the hard–soft interaction of TAA with cadmium and lead ions seems to be inverted. Arguments for this inversion can be found in the different ionic species and concentrations or in the different decomposition rate of the deprotonated intermediates.

As in the Pb–TAA reaction the initial metal concentration is only one-tenth that in the other solutions and as no chloride ions are present, the results of the Cd–TAA and Co–TAA interactions were extrapolated to an

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initial cadmium and cobalt chloride concentration of 1.8×10^{-3}M. In these acetate buffered solutions, with the metal ion almost entirely present as monoacetate complex, the sequence of reactivity with TAA remains $PbOAc^+ > CdOAc^+ > CoOAc^+$.

Assuming that the acetate ion increases the soft character of the metal ions in the same proportion, the observed inversion can not be explained on the basis of stability constants alone and should result from the greater decomposition rate of PbOAcTAA with regard to CdOAcTAA.

Since both hydrogen ion and metal ion are acids, it might be expected that the same mechanism applies on the basis of their catalytic action. This is not so because the hydrogen ion catalysed reaction leads initially to acetamide and thioacetic acid [9] while the metal promoted reaction produces acetonitrile. The difference in mechanism probably results from the much smaller electron draining effect toward the side of attachment with H_3O^+ than with the studied metals. Formation of the enol form of TAA from the *S*-protonated TAA [reaction (18)] and subsequently formation of acetonitrile [(19)] must be less favourable than reactions (9)—(14).

$$CH_3C(NH_2){:}\overset{+}{S}H + H_2O \rightleftharpoons CH_3C({:}NH)SH + H_3O^+ \qquad (18)$$

$$CH_3C({:}NH)SH + H_2O \longrightarrow CH_3CN + HS^- + H_3O^+ \qquad (19)$$

By analogy with the proposed mechanism for thiobenzamide [21] the hydrogen ion catalysed hydrolysis of TAA can be understood by a nucleophilic attack of H_2O on the thiocarbonyl carbon with formation of a tetrahedral intermediate.

$\log k_{obs}$–pH diagrams for the present and previous [9] data indicate that, if both hydrogen ion and Pb^{2+}, Cd^{2+}, or Co^{2+} are present, the hydrogen ion catalysed mechanism predominates at pH < 3 while at higher pH the metal ion catalysed mechanism is the more important one.

Hall and Satchell studied the reaction between thiobenzamide and mercury(II),[22] copper(II),[23] and silver(I) [24] ions in perchlorate medium at pH < 3. The organic product was benzonitrile and the obtained rate equation corresponds in part with equation (16). A mechanism quite similar to that proposed in this work was given. The order of reactivity, Hg > Ag > Cu, is in agreement with the HSAB principle.

These results and those obtained in this study show that the order of reactivity of metal ions with a thioamide group, except for the inversion of Cd and Pb, is in general predictable from the hardness–softness character of the metal ions involved.

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