

Kinetics of the Mercury(II) Ion-promoted Desulfurisation of Thiocarbamates in Aqueous Solution

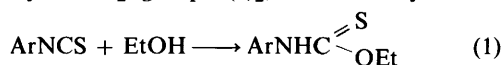
Derek P. N. Satchell,^{*,a} Rosemary S. Satchell^a and Wasfy N. Wassef^b

^a King's College London, Strand, London WC2R 2LS, UK

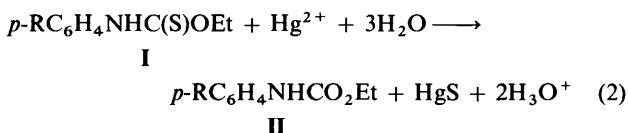
^b Ain-Shams University, Heliopolis, Cairo, Egypt

In a 1% dioxane–water solvent in the presence of Hg^{2+} ions thiocarbamates $p\text{-RC}_6\text{H}_4\text{NHC(S)OEt}$ ($\text{R} = \text{MeO}, \text{Me}, \text{H}, \text{F}$) rapidly form complexes of 2 thiocarbamate: 1 Hg^{2+} stoichiometry. In the presence of an excess of Hg^{2+} ions partial conversion to the 2:2-complexes probably occurs which decompose to the corresponding carbamates ($p\text{-RC}_6\text{H}_4\text{NHCO}_2\text{Et}$) and HgS . With $\text{R} = \text{NO}_2$ the 2:2 complex is dominant even at low Hg^{2+} ion concentrations, and desulfurisation is then independent of $[\text{Hg}^{2+}]$. Electron-withdrawal by R favours the 2:2 complex but decreases its rate of decomposition to products. The effects of changes in the hydrogen ion concentration suggest that ionisation of N-bound protons in the complexes favours reaction. A mechanism is suggested. The kinetic behaviour is somewhat similar to that found previously for thiobenzamides, but the new results suggest the mechanism previously proposed may need revision.

Thiocarbamates, the products of addition of alcohols to aryl or alkyl isothiocyanates [e.g. eqn. (1)], are relatively stable in



dilute aqueous acid, and are known to form stable complexes with Ag^+ ions.¹ We have now studied for the first time the kinetics of their decomposition in dilute aqueous acid promoted by Hg^{2+} ions; their reaction leads to the corresponding carbamate [eqn. (2)]. Few kinetic studies exist of the



desulfurisation of thiocarbonyl groups using Hg^{2+} ions.²

Experimental

Materials.—Thiocarbamates (**I**, $\text{R} = \text{MeO}, \text{Me}, \text{H}, \text{F}, \text{NO}_2$) were prepared from the corresponding isothiocyanates (Aldrich) and an excess of ethanol by standard methods.^{3,4} Carbamates **II** were similarly prepared from the isocyanates (Aldrich). All compounds had appropriate NMR spectra. The thiocarbamates (except the nitro-derivative which absorbs at 335 nm) have absorption maxima in the region 260–280 nm, where the carbamates absorb much less strongly.

Perchloric acid and sodium perchlorate were of AnalaR grade, and dioxane was the Aldrich spectroscopic grade. Solutions of mercury(II) perchlorate were prepared as before.⁵

Reaction Products.—In a dioxane–water mixture containing perchloric acid (0.1–0.5 mol dm^{-3}), and an excess of mercury(II) perchlorate, the thiocarbamates lead eventually to an effectively quantitative yield of the corresponding carbamates, as determined by changes in UV spectra. Carbamate and HgS were also isolated in good yield from preparative-scale reactions. There is no evidence for reversion to isothiocyanate, or for formation of ArNH_2 (e.g. via thiocarbamic acid formation).¹

Complex Formation.—The production of **II** at low values of $[\text{Hg}^{2+}]$ is slow enough to permit some spectroscopic study of

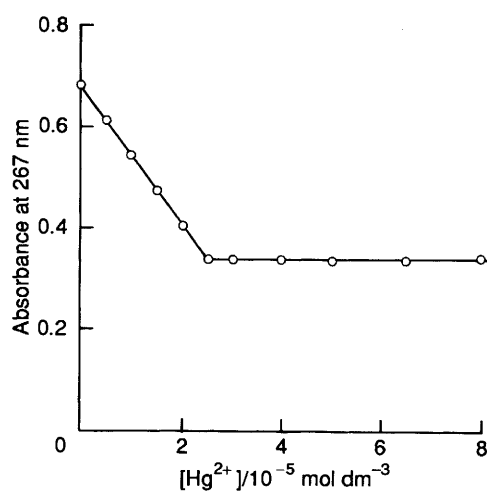


Fig. 1 Complex formation between **I** ($\text{R} = \text{OMe}$) and Hg^{2+} ions. $[\text{Thiocarbamate}]_{\text{initial}} = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$.

complex formation between **I** and Hg^{2+} ions. When Hg^{2+} ions are added to a solution of **I** ($\text{R} = \text{MeO}, \text{Me}, \text{H}, \text{F}$) there is an instantaneous reduction in the absorption due to **I** and, with $[\text{I}] \sim 5 \times 10^{-5} \text{ mol dm}^{-3}$, Job's method⁶ shows that all the thiocarbamates form 2:1 Hg^{2+} complexes stoichiometrically in the presence of Hg^{2+} ions (e.g. Fig. 1). The spectra of the 2:1 complexes, which mostly have a shoulder-like absorption in the 260–280 nm region, have intensities about half those of the free thiocarbamates at the absorption maxima of the latter. With **I** ($\text{R} = \text{NO}_2$), however, the band centred at 335 nm is first converted to a less intense broad band at 355 nm (the 2:1 complex) which is progressively transformed into a band at 310 nm as $[\text{Hg}^{2+}]$ is raised. This corresponds to rapid conversion into a second complex of perhaps 1:1 stoichiometry. The decomposition of this second complex to carbamate (at 322 nm) makes measurements of its equilibrium formation difficult, but it is probably largely formed when $[\text{Hg}^{2+}] > 10^{-3} \text{ mol dm}^{-3}$. Some slight evidence of further complex formation by the $p\text{-F}$ derivative can also be detected.

Kinetics.—All reactions were studied using a large excess of Hg^{2+} ions. The observed slow process was therefore the loss of

Table 1 Values of k_{obs} , k and K (a) Effects of acid concentration, ionic strength and temperature on k_{obs} ^a

R in <i>p</i> -RC ₆ H ₄ NHC(S)OEt	<i>T</i> /°C	[Hg ²⁺]/10 ⁻³ mol dm ⁻³	[H ₃ O ⁺]/mol dm ⁻³	<i>I</i> /mol dm ⁻³	$k_{\text{obs}}/10^{-2}$ min ⁻¹				
MeO	25.0	8.00	0.10	0.50	15				
			0.20		7.0				
			0.30		5.9				
			0.40		4.1				
		4.00	0.48	0.11	3.3				
			0.10		4.2				
			0.20		5.8				
			0.30		6.7				
			0.50		7.5				
			Me		25.0	8.00	0.10	0.50	10
							0.20		6.0
							0.30		4.0
0.40	3.3								
0.48	2.7								
0.10	3.9								
H	25.0	8.00	0.10	0.50	6.1				
			0.20		4.3				
			0.30		3.5				
			0.48		2.5				
		4.00	0.10	0.11	3.1				
			0.20		3.9				
			0.30		4.2				
			0.50		4.6				
			F		25.0	8.00	0.10	0.50	6.5
							0.20		4.2
							0.30		3.4
							0.48		2.4
4.00	0.10	0.11		2.4					
	0.20			2.7					
	0.30		3.0						
	0.50		3.8						
NO ₂	25.0	8.00	0.10	0.50	11				
			0.20		10				
			0.30		12				
			0.48		9.3				
		4.00	0.10	0.11	9.0				
			0.20		9.4				
			0.30		9.7				
			0.50		10				
			14.5		4.00	0.10	0.50	3.0	
							30.0	17	
							35.0	23	

(b) Derived constants for eqn. (7)

R in <i>p</i> -RC ₆ H ₄ NHC(S)OEt	$k/10^{-2}$ min ⁻¹	K
NO ₂	10	> 1000
F	25	45
H	30	33
Me	70	21
MeO	125	11

^a [RC₆H₄NHC(S)OEt]_{initial} ≈ 3 × 10⁻⁵ mol dm⁻³; solvent = 1% (v/v) dioxane-water; k_{obs} = observed first-order rate constant; I = ionic strength; $\Delta H^\ddagger = 73 \pm 5$ kJ mol⁻¹; $\Delta S^\ddagger = -56 \pm 5$ J K⁻¹ mol⁻¹.

the rapidly-formed thiocarbamate-Hg²⁺-complex (or complexes). The fall in absorption of the complexes was monitored, at various fixed mercury(II) and hydrogen ion concentrations, at constant ionic strength (NaClO₄). The solvent for the kinetic runs was 1% (v/v) dioxane-water and reaction initiated by the addition of a small volume of a stock solution of **I** in dioxane to give [**I**]_{initial} 3 × 10⁻⁵ mol dm⁻³. Reactions were first order over at least three half-lives, and the observed first-order rate constant, k_{obs} , was reproducible to within ±15%. Reaction mixtures remained homogeneous throughout a run. The rates of hydrolysis of the thiocarbamates in the absence of Hg²⁺ ions,

and of the reactions of **II** in typical reaction mixtures, were negligible compared with the measured rates. Our various concentration and other conditions are in Table 1 and Figs. 1–3. Most experiments were performed at 25 °C.

Results and Discussion

The initial concentration of thiocarbamate in the kinetic runs was ca. 3 × 10⁻⁵ mol dm⁻³, and the minimum concentration of Hg²⁺ ions was 5 × 10⁻⁴ mol dm⁻³. The experiments on complex formation show that under such conditions all the

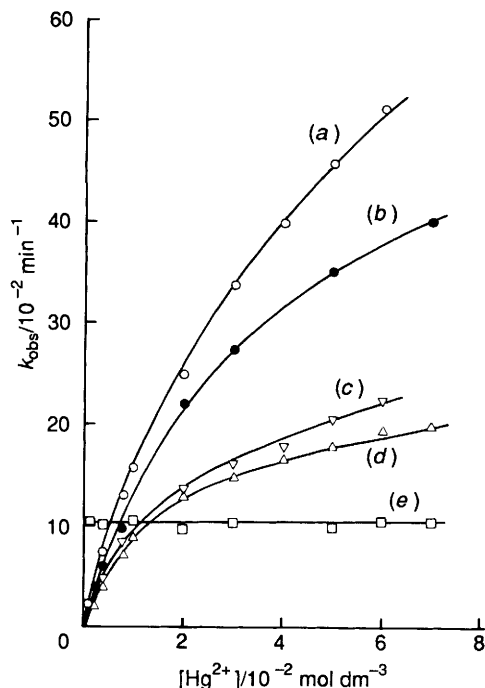


Fig. 2 Dependence of k_{obs} on $[Hg^{2+}]$ at 25 °C. [Thiocarbamate] $_{initial} \approx 3 \times 10^{-5}$ mol dm $^{-3}$; $[H_3O^+] = 0.10$ mol dm $^{-3}$; ionic strength = 0.50 mol dm $^{-3}$; solvent = 1% (v/v) dioxane–water; (a) MeO; (b) Me; (c) H; (d) F; (e) NO $_2$.

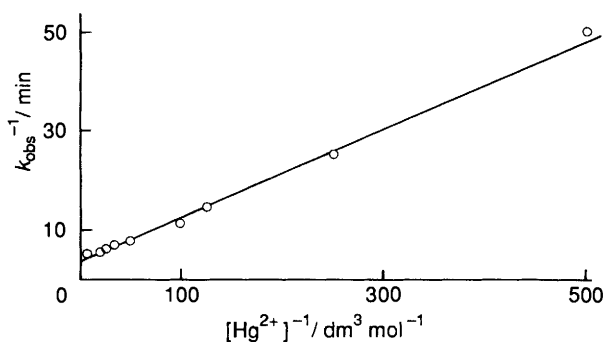
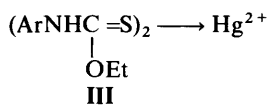


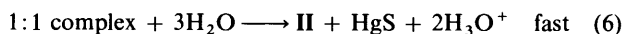
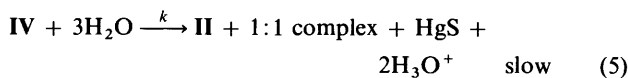
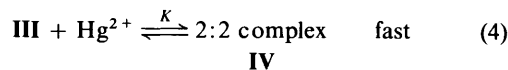
Fig. 3 Plot of eqn. (8) for I (R = F)

thiocarbamates, except the NO $_2$ -derivative, will exist in solution predominantly as their 2:1 complexes; the NO $_2$ derivative is probably largely converted into a complex of 1:1-stoichiometry when $[Hg^{2+}] \approx 10^{-3}$ mol dm $^{-3}$. In aqueous solution the simplest likely structure for the 2:1 complex (omitting water molecules) is III, based on soft–soft interactions; chelation involving both S and N is also conceivable. These conclusions follow from existing knowledge of complex formation between thioamides, and similar compounds, and soft and other metal ions.⁷ In particular it is found that *N*-substituted thioamides can exhibit bidentate behaviour.



The effect on k_{obs} at 25 °C of increases in $[Hg^{2+}]$ at fixed values of $[H_3O^+]$ and ionic strength are shown in Fig. 2. For the MeO, Me, H and F-derivatives, k_{obs} increases with $[Hg^{2+}]$ in a manner suggestive of further complex formation. The effect is most marked for the F-derivative. With I (R = NO $_2$), k_{obs} is independent of $[Hg^{2+}]$ when this concentration $> 10^{-3}$ mol dm $^{-3}$. The pattern of results immediately suggests that the 2:1 complexes of the MeO, Me, H and F-derivatives are being

progressively converted to 1:1 complexes when $[Hg^{2+}] > 5 \times 10^{-4}$ mol dm $^{-3}$, and that these complexes are much more reactive than the 2:1 complexes, and decompose without further involvement of Hg $^{2+}$ ions, as does the complex formed by the NO $_2$ -derivative. Such a mechanism, eqns. (3)–(6), is



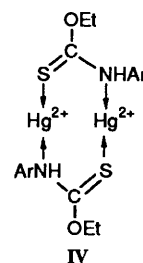
compatible with the kinetic details provided that the second complexes have a 2:2, rather than a 1:1, stoichiometry. For eqns. (3)–(6), k_{obs} is given by eqn. (7), a form compatible with the results in Fig. 2.

$d[\text{II}]/dt = k[\text{IV}] = -d[\text{III}]_t/dt = k_{obs}[\text{III}]_t$ and $[\text{IV}] = K[\text{Hg}^{2+}][\text{III}]_t/(1 + K[\text{Hg}^{2+}])$ where $[\text{III}]_t$ is the total concentration of free and complexed III at any time *i.e.* $[\text{III}] + [\text{IV}]$.

$$\therefore k_{obs} = kK[\text{Hg}^{2+}]/(1 + K[\text{Hg}^{2+}]) \quad (7)$$

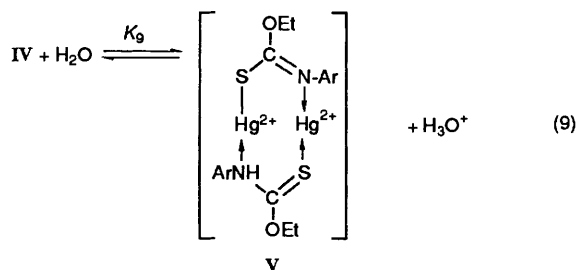
$$\text{or } 1/k_{obs} = 1/kK[\text{Hg}^{2+}] + 1/k \quad (8)$$

Plots of $1/k_{obs}$ *vs.* $1/[Hg^{2+}]$ are reasonably rectilinear (*e.g.* Fig. 3), and provide approximate values of k and K (Table 1). The assumed direct and rapid formation of (two) 1:1 complexes in equilibrium (4) leads to the prediction of a more complicated kinetic form than that observed ($[\text{IV}]$ then depends upon $[Hg^{2+}]^2$), and is incompatible with results in Fig. 2. A possible structure for the 2:2 complex IV is



Complexes of 2:2 stoichiometry between thioamides and mercury(II) species are known.⁸

The effects of changes in $[H_3O^+]$ on k_{obs} (Table 1) suggest, however, that the actual mechanism is certainly more complicated than the outline mechanism of eqns. (3)–(6). As $[H_3O^+]$ is increased k_{obs} decreases. This effect is most marked for the MeO



derivative (Table 1). It suggests that the complexes may ionise

via loss of N-bound protons, and that the deprotonated form of IV [eqn. (9)] is more reactive than IV itself. That is likely, since the loss of this proton is probably necessary before the C-S bond can be cleaved by attack of water. Indeed, the low reactivity of the 2:1 complexes III and of the Ag⁺ complexes,¹ may arise from relatively difficult loss of protons from those complexes. A revised outline mechanism including eqn. (9), and making the simplifying assumption that the reactivity of V is much greater than that of IV, leads to an expression for k_{obs} of the same form as eqn. (7) but with K replaced by $kK_9/([\text{H}_3\text{O}^+] + K_9)$ and with k referring to the slow decomposition of V rather than IV. The results are insufficient for the separate estimation of K and K_9 , especially in view of the simplifying assumption made. Qualitative considerations suggest that increased electron release by R will reduce both K and K_9 , whereas opposing effects may operate in step (5) (easier C-S cleavage but more difficult attack by water). Electron release is therefore predicted to lower the observed equilibrium constant (at constant $[\text{H}_3\text{O}^+]$), and to affect it more than k . This is found (Table 1). The dominant effect on k appears to be that on C-S cleavage.

For the NO₂-derivative, $[\text{H}_3\text{O}^+]$ has little effect on k_{obs} , and IV may be largely ionised to V for this compound. If so, the effects of temperature on k_{obs} (Table 1) will apply directly to the decomposition of V in a step analogous to step (5). The effects of changes in ionic strength (Table 1) are rather small, and might have been expected to be larger in view of the charged nature of the reactants. However, a very similar result was obtained earlier with thiobenzamides.⁹

Thiocarbamates are both thioesters and thioamides. It is interesting therefore that our present results are reminiscent of those found earlier for thiobenzamide and *N*-cyclohexyl thiobenzamide under similar conditions.⁹ These thioamides also lead to the rapid and stoichiometric formation of 2 thioamide: 1Hg²⁺ complexes whose rate of decomposition to the desulphurised product (PhCN and PhCONHC₆H₁₁, respectively) is promoted by an excess of Hg²⁺ ions, and falls as $[\text{H}_3\text{O}^+]$ rises. A significant difference between these earlier

results and those for the present system is that only rectilinear plots of k_{obs} vs. $[\text{Hg}^{2+}]$ passing through the origin were found, in contrast to the curved plots of Fig. 2. In other words there was no experimental evidence with the thiobenzamides for the rapid, equilibrium formation of significant quantities of complexes of 2:2 (or 1:1) stoichiometry, and a mechanism involving a slow reaction of Hg²⁺ ions with the 2:1-complexes was proposed.⁸ The present mechanism provides an alternative.

In the presence of a given excess of Hg²⁺ ions the thiobenzamides are more reactive than the present thiocarbamates.⁹ *O*-Ethyl thiobenzoates [ArC(S)OEt] are very much more easily desulfurised,¹⁰ so the insertion of an NH group must have a powerful stabilising effect on the C=S → Hg²⁺ complexes formed, which may reflect chelation for the N-containing complexes.

References

- 1 L. Drobnica, P. Kristian and J. Augustine, in *The Chemistry of Cyanates and their Thio Derivatives*, ed. S. Patai, part 2, ch. 22, Wiley, Chichester, 1977.
- 2 D. P. N. Satchell, *Chem. Soc. Rev.*, 1977, 3, 345.
- 3 D. W. Browne and G. M. Dyson, *J. Chem. Soc.*, 1934, 178.
- 4 C. N. R. Rao and R. Venkataraghavan, *Tetrahedron*, 1963, 19, 1509.
- 5 D. Penn and D. P. N. Satchell, *J. Chem. Soc., Perkin Trans. 2*, 1982, 813.
- 6 D. P. N. Satchell and T. J. Weil, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1191.
- 7 *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, A. D. Gillard and J. A. McCleverty, Pergamon Press, Oxford, 1987, vol. 2, pp. 647, 804.
- 8 S. Ishikawa, *Chem. Zentr.*, 1928, 98, 1765.
- 9 A. J. Hall and D. P. N. Satchell, *J. Chem. Soc., Perkin Trans. 2*, 1975, 778.
- 10 D. P. N. Satchell, M. N. White and T. J. Weil, *Chem. Ind.*, 1975, 791.

Paper 2/007501

Received 12th February 1992

Accepted 20th March 1992