The Chemistry of Niobium and Tantalum Dithiocarbamato-complexes. Part 6.[1] The Kinetics and Mechanism of the Hydrazine-forming Reactions between $[\{Ta(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$ and HBr: Cleavage of the Binuclear Unit

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The kinetics of the reaction between $[\{Ta(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$ and an excess of HBr in MeCN, to yield hydrazine and $[TaBr_2(S_2CNEt_2)_3]$, have been studied. The reaction involves the rapid formation of the intermediate $[(Et_2NCS_2)_3Ta(\mu\text{-}NHNH_2)TaBr(S_2CNEt_2)_3]^{2+}$, which subsequently undergoes rate-limiting tantalum–nitrogen bond cleavage to give $[TaBr(S_2CNEt_2)_3]^+$ and $[Ta(NHNH_2)(S_2CNEt_2)_3]^+$. The former complex rapidly picks up Br^-, and the latter is further protonated to yield hydrazine and the second mole equivalent of the dibromo-product ultimately.

We have already shown[1] that in many of the hydrazine-forming reactions of acid with $[\{M(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$ (M = Nb or Ta) in MeCN the rate-limiting step is protonation of the dinitrogen ligand. Nothing, however, is known with any certainty about the cleavage of the binuclear units in bridging dinitrogen complexes upon protonation, in either our own systems or any other.[2] In this paper we describe mechanistic studies on the reaction between $[\{Ta(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$ and HBr in MeCN in which we can detect, spectrophotometrically, $[(Et_2NCS_2)_3Ta(\mu\text{-}N_2H_3)TaBr(S_2CNEt_2)_3]^{2+}$, the species which undergoes unimolecular tantalum–nitrogen cleavage.

Results

The reaction between $[\{Ta(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$ and an excess of HBr proceeds according to the stoicheiometry shown in equation (1), where the metal-containing product $[TaBr_2(S_2CNEt_2)_3]$ has been structurally characterised by *X*-ray crystallography.[3] The kinetics of reaction (1) were studied by stopped-flow spectrophotometry in the range λ = 350—500 nm. The reaction occurs in two phases: an initial rapid absorbance increase (complete within the dead-time of the stopped-flow apparatus, 3.3 ms), to yield an intermediate whose spectrum is shown in Figure 1, followed by an exponential decay to yield the products.

$$[\{Ta(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)] + 4HBr \longrightarrow 2[TaBr_2(S_2CNEt_2)_3] + N_2H_4 \quad (1)$$

The stoicheiometry of the intermediate was established by showing that the initial absorbance jump reached its maximum amplitude only when ⩾3 mole equivalents of HBr were present as shown in Figure 1 (insert).

The kinetics of decay of the intermediate exhibits a first-order dependence on the concentration of the intermediate, but a complicated dependence on the concentration of HBr, as shown by the data in the Table and Figure 2. The addition of $[NBu^n_4]Br$ inhibits the reaction as shown by the data in the Table. However, in aprotic solvents the introduction of a salt to an acid solution effectively decreases the concentration of acid because of the perturbation afforded to the homoconjugation ($K_{Br} = 2.51 \times 10^2$ dm^3 mol^{-1})[4] and acid–base equilibria ($K_a = 3.16 \times 10^{-6}$)[4] shown in equations (2) and (3) respectively.

$$HBr + Br^- \underset{}{\overset{K_{Br}}{\rightleftharpoons}} HBr_2^- \quad (2)$$

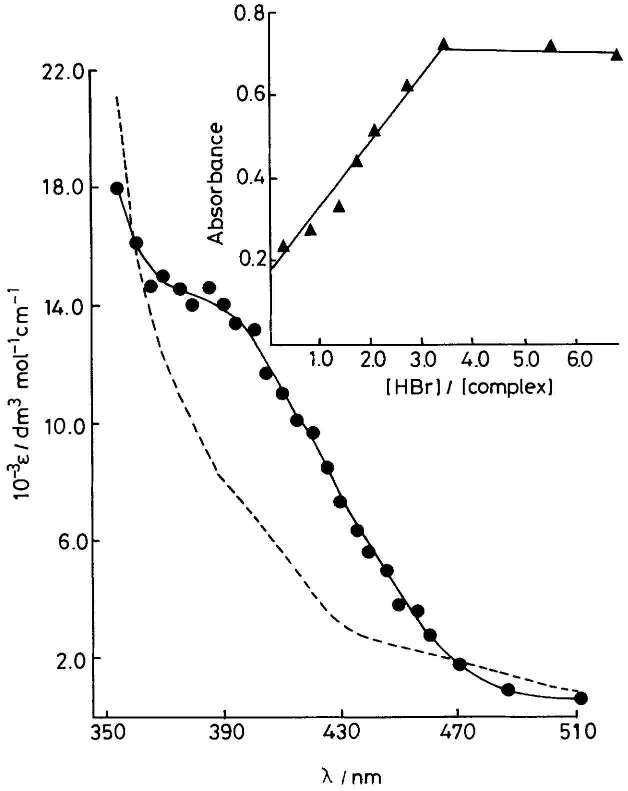


Figure 1. Visible absorption spectrum of $[(Et_2NCS_2)_3Ta(\mu\text{-}NHNH_2)TaBr(S_2CNEt_2)_3]^{2+}$ detected in the reaction of $[\{Ta(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$ with HBr in MeCN. The dashed line shows the spectrum of $[\{Ta(S_2CNEt_2)_3\}_2(\mu\text{-}N_2H)]^+$ detected in the corresponding reactions with HCl. Insert: spectrophotometric determination of the stoicheiometry of the intermediate detected in the reaction of $[\{Ta(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$ (1.0×10^{-5} mol dm^{-3}) with HBr (λ = 420 nm)

$$HBr + MeCN \overset{K_a}{\rightleftharpoons} MeCNH^+ + Br^- \quad (3)$$

Allowing for these perturbations and hence calculating the concentrations of 'free' HBr, the kinetic data, for the studies in the presence of $[NBu^n_4]Br$, define the same curve as in the studies where no bromide salt was introduced. All these data are plotted in Figure 2. Analysis of the kinetic data by the usual 'double reciprocal plot'[5] results in the rate equation (4), where

Table. Kinetic data for the reaction between $[\{Ta(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$ (2.5×10^{-5} mol dm^{-3}) and HBr in MeCN (25.0 °C, ionic strength = 0.1 mol dm^{-3}, $[NBu^n_4][BF_4]$, λ = 420 nm)

[HBr][a]/mmol dm^{-3}	[Br$^-$][a,b]/mmol dm^{-3}	$k_{obs.}$[c]/s^{-1}
2.0		5.0 (5.2)
3.0		6.3 (6.1)
5.0		8.8 (8.8)
6.0		9.5 (9.2)
10.0		10.5 (10.5)
15.0		11.5 (11.2)
20.0	5.0	12.3
	20.0	12.7
	30.0	10.5
	40.0	9.8
2.0	1.0	5.2
	2.0	4.4
	5.0	3.9
	8.0	3.6
	10.0	3.5
2.5	10.0	2.7
5.0		6.4
10.0		9.7
15.0		11.5
20.0		12.3
2.5	20.0	2.5
5.0		5.0
10.0		8.8
15.0		10.5
20.0		12.9
1.0	1.0	2.6
2.0	2.0	4.3
4.0	4.0	6.5
7.5	7.5	9.4
10.0	10.0	11.3
5.0[d]		9.1
5.0[e]		9.0

[a] Concentrations of HBr and Br$^-$ shown are those added to the reaction mixture. The concentrations plotted in Figure 2 are corrected for the homoconjugation and acid–base equilibria of equations (2) and (3) respectively, and the consumption of 3 mole equivalents of HBr to form the detected intermediate. [b] Bromide supplied as $[NBu^n_4]Br$. [c] Values in parentheses are the rate constants measured using DBr. [d] 5.0×10^{-5} mol dm^{-3} $[\{Ta(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$. [e] 1.3×10^{-5} mol dm^{-3} $[\{Ta(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$.

$$k_{obs.} = \frac{(5.5 \pm 0.8) \times 10^3[\text{HBr}]}{1 + (3.5 \pm 0.4) \times 10^2[\text{HBr}]} \tag{4}$$

$k_{obs.}$ is the rate constant observed under pseudo-first-order conditions. Studies using DBr revealed no detectable isotope effect.

Discussion

Before any mechanistic interpretation can be made on the kinetics observed in this system, it is essential to have a clear idea about the formulation of the spectrophotometrically detected intermediate. That 3 mole equivalents of HBr are consumed by $[\{Ta(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$ to form the intermediate (Figure 1) indicates that this species is either derived from $[\{Ta(S_2CNEt_2)_3\}_2(\mu\text{-}NHNH_2)]^{3+}$ or $[Ta(NHNH_2)(S_2CNEt_2)_3]^+$. In the latter case the mononuclear species is clearly formed as a consequence of rapid tantalum–nitrogen bond cleavage, together with 1 mole equivalent of the product $[TaBr_2(S_2CNEt_2)_3]$. On the basis of the stoicheiometry alone it is impossible to distinguish between these two possibilities.

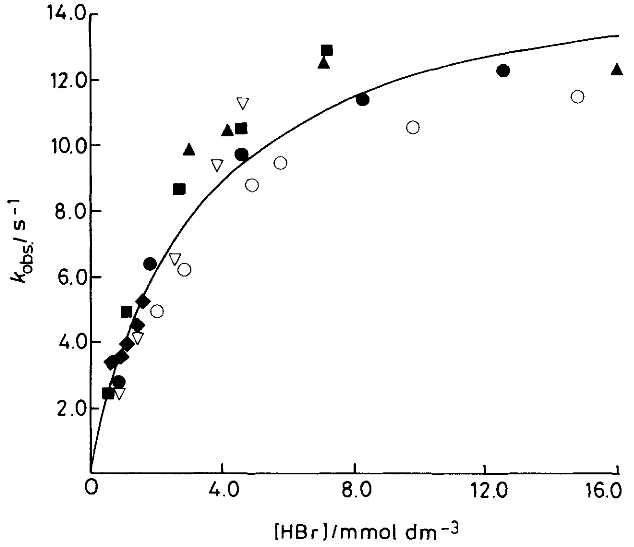
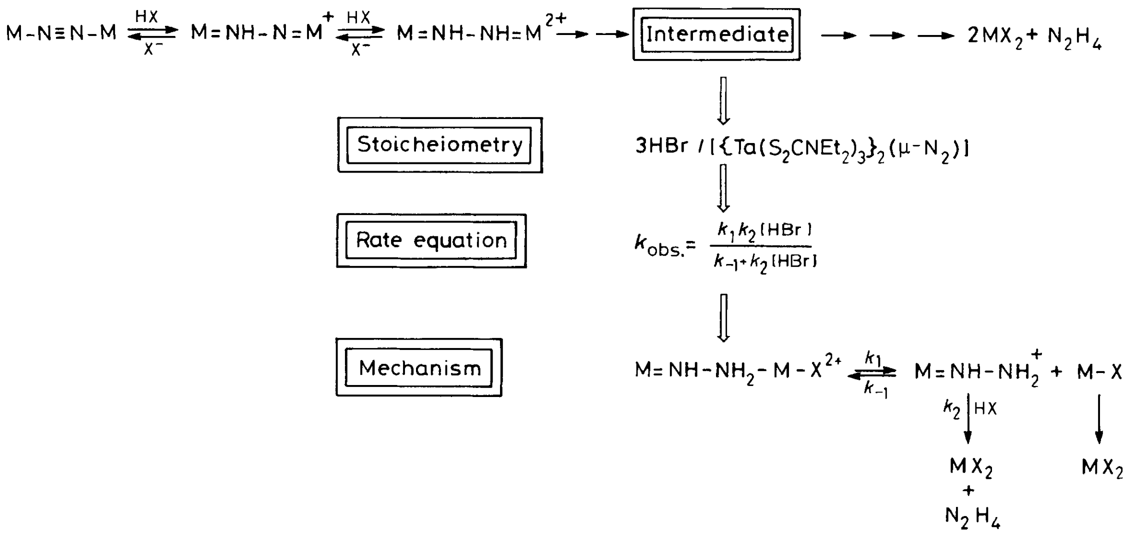


Figure 2. Kinetic data for the decomposition of the intermediate detected in the reaction between $[\{Ta(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$ (2.5×10^{-5} mol dm^{-3}) and HBr in MeCN at 25 °C. The concentrations of acid plotted have been corrected for the homoconjugation and acid–base equilibria shown in equations (2) and (3) and the consumption of 3 mole equivalents of HBr to form the intermediate. Data points shown correspond to [HBr] = 2.0—15.0 (○); [HBr] = 20.0, [Br$^-$] = 5.0—40.0 (▲); [HBr] = 2.0, [Br$^-$] = 1.0—10.0 (◆); [HBr] = 2.5—20.0, [Br$^-$] = 10.0 (●); [HBr] = 2.5—20.0, [Br$^-$] = 20.0 (■); and [HBr] = 1.0—10.0, [Br$^-$] = 1.0—10.0 mmol dm^{-3}; [HBr]/[Br$^-$] = 1.0 (▽). The curve drawn is that defined by equation (4)

The kinetics for the decay of the intermediate described by equation (4) is consistent with a mechanism involving a rate-limiting unimolecular reaction followed by rapid protonation. In particular, the absence of any bromide-dependent terms in the rate law precludes a protonation reaction prior to the rate-limiting step. It is difficult to rationalise the rate equation (4) with the expected reactivity of the mononuclear hydrazide proposed above as the detected intermediate. Such a complex might contain the hydrazido(1 −)-ligand bound end-on or side-on. If the hydrazido(1 −)-ligand were co-ordinated end-on (Ta–NH–NH$_2$) then it is difficult to visualise what the rate-limiting unimolecular reaction, which precedes the protonation step, might be. The reactivity pattern expected of a side-on bound hydrazido(1 −)-ligand $(\overline{\text{TaNHN}}\text{H}_2)$ has already been established[6] using $[\overline{\text{TaNMeN}}\text{Me}_2)(S_2CNEt_2)_3]^+$. The reaction of the latter complex with HBr in MeCN exhibits very different kinetics to that described by equation (4), with rate-limiting ring opening which is some 10^3 times slower than that necessary to rationalise the reactivity of this type of ligand with the rate equation (4). We therefore propose that the reaction between $[\{Ta(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$ and an excess of HBr proceeds *via* the spectrophotometrically detected $[(Et_2NCS_2)_3Ta(\mu\text{-}NHNH_2)TaBr(S_2CNEt_2)_3]^{2+}$ as summarised in the Scheme. It should be noted that $k_{obs.}$ is independent of the concentration of binuclear complex (Table), which must indicate that upon cleavage the two metal fragments are still associated (possibly *via* hydrogen bonding). Further detailed analysis of this cleavage step is precluded by the multistep nature of the formation of the detected intermediate. Comparison of the derived rate equation shown in the Scheme with equation (4) allows the determination of $k_1 = 15.7 \pm 0.5$ s^{-1} (the elementary rate constant for tantalum–nitrogen bond cleavage) and $k_2/k_{-1} = (3.5 \pm 0.4) \times 10^2$.

The results of the study described herein, together with the



Scheme. Summary of the evidence assigning the nature of the intermediate detected in the reaction between $[\{Ta(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$ and HBr in MeCN. Dithiocarbamato-ligands omitted for clarity

previous studies[1] on the $[\{M(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$ (M = Nb or Ta) system allow a relatively detailed picture of the mechanism of hydrazine formation from binuclear complexes to be drawn (Scheme). Thus in several of the reactions studied, such as that between $[\{Ta(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$ and HCl, the rate-limiting step is the initial protonation of the bridging dinitrogen residue.[1] The second protonation has been proposed to yield the diazene species. The third proton must now bind at an already protonated nitrogen atom to yield $[\{M(S_2CNEt_2)_3\}_2(\mu\text{-}NHNH_2)]^{3+}$. At this stage one of the '$M(S_2CNEt_2)_3$' units (the one bonded to the NH_2 end of the bridging hydrazide) is very electron deficient and thus binds an anion prior to the cleavage of the binuclear species. It is this cleavage step that can be observed in the reactions of HBr with $[\{Ta(S_2CNEt_2)_3\}_2(\mu\text{-}N_2)]$. Upon cleavage $[Ta(NHNH_2)(S_2CNEt_2)_3]^+$ and $[TaBr(S_2CNEt_2)_3]^+$ are formed, and the latter rapidly binds bromide to yield $[TaBr_2(S_2CNEt_2)_3]$, whilst the former is rapidly protonated to yield hydrazine and the second mole equivalent of the dibromo-product.

Probably the most important aspect of the work described herein is the demonstration that a bridging dinitrogen ligand can bind three protons before the binuclear unit breaks up. Clearly, after rupture of a tantalum–nitrogen bond, the factors effecting the protonation of the nitrogenous ligands are those for mononuclear systems, which have been defined already.[7–9] Although as many as three protons can bind to the bridging dinitrogen ligand in the systems described in this series of papers, it requires further studies to establish whether this pattern persists in other binuclear complexes.

Experimental

All materials, manipulations, and kinetic studies were performed as described before.[1]

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Received 12*th May* 1989; *Paper* 9/01993F