Reactions of Organosulphur Ligands on Tungsten Centres. Evidence for Carbonium Ion Formation in the Degradation of Alkanethiolatopentachlorotungsten(VI) Species

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The monothiolate derivatives of tungsten(VI) chloride, [$WCl_5(SR)$] (R = Me, Et, cyclohexyl, Bu^i, Bu^t, CH_2Ph, or Ph), have been found to be unstable with respect to at least two modes of degradation. Heterolytic cleavage of the carbon–sulphur bond to generate a carbonium ion, which can further abstract chloride to give $WSCl_4$ + RCl, is the preferred pathway if the R^+ ion is relatively stable. The intermolecular elimination of R_2S_2 is the alternative route for degradation and is the exclusive one for R = Ph, where the carbonium ion is very unstable. The only pure [$WCl_5(SR)$] compounds which have been isolated are [$WCl_5(SMe)$] and [$WCl_5(SPh)$] and even these slowly decompose at room temperature over a period of a few weeks.

THE reactions of co-ordinated organosulphur species are important for several reasons. First, there is interest in this area of chemistry as it relates to heterogeneous catalysis. Many different metal compounds show reactivity as catalysts for hydrodesulphurization.[1] Secondly the chemical environments of iron, molybdenum, and copper in certain biological systems have either been proven to contain thiolato-groups[2] or at least strong circumstantial evidence supports such speculation.[3] Indeed it seems probable that examples will be found of other heavy metals whose biological attachment involves sulphur-containing amino-acid residues. To date, much of the inorganic chemistry of relevance to biological systems has involved the synthesis, characterization, and redox properties of model systems, such as metal–sulphide–thiolate clusters.[2,4] Relatively little has been done on the reactions of a metal–sulphur–carbon bonded system itself. Of the published work on this topic that of Deutsch and coworkers[5] is of particular interest since they have reported a number of chemical oxidation studies of thiolato-complexes. The most common reaction of thiolato-complexes is undoubtedly the reductive elimination of dialkyl disulphides from the metal centres,[5,6] although, of course the hydrolysis reaction to yield RSH is also well established.

We recently reported briefly the synthesis of a number of thiolato-complexes of molybdenum and tungsten, obtained by reaction of an appropriate metal chloride with stoicheiometric amounts of alkylthiotrimethylsilane.[7] Many of the compounds produced showed a reduction in the metal oxidation state, indicative of the thermodynamic instability of W^{VI}–SR, W^{V}–SR, and Mo^{V}–SR moieties towards reductive elimination of R_2S_2. Of more interest, however, was the observation of elimination of RCl from several members of the series [$WCl_5(SR)$] where R = alkyl or aryl. The stability sequence for varying R groups suggested that the R group was heterolytically cleaved yielding a carbonium ion. In this paper we report a detailed study of this series of compounds aimed at establishing the mechanism(s) by which degradation occurs. In particular the activation of the S–R bond towards loss of an R^+ ion has been studied, both in solution and by thermal degradation of solid samples.

RESULTS

Synthesis and Characterization.—The synthesis of the [$WCl_5(SR)$] series of compounds was attempted by reaction (1). The choice of solvent was restricted to poor-donor

$$WCl_6 + SiMe_3(SR) \longrightarrow [WCl_5(SR)] + SiMe_3Cl \qquad (1)$$

organic compounds with low dielectric constants, of which CS_2 and CH_2Cl_2 were found most convenient. Although evidence has been presented by other workers[8] for insertion of CS_2 into M–SR bonds to form thioxanthates, there was no evidence for this reaction occurring in our systems. Since much of the work involved ^1H n.m.r. spectral studies of the reaction solutions, CS_2 was the more suitable solvent of the two, and was used for the bulk of the work reported here.

Of the wide range of R groups studied (R = Me, Et, Bu^i, Bu^t, cyclo-C_6H_{11}, Ph, or CH_2Ph) only in the cases of R = Me and Ph was it possible to isolate compounds analyzing as [$WCl_5(SR)$]. The characterization of these compounds is given in the Experimental section. In order to isolate even these two compounds the products had to be removed from solution as rapidly as possible, before degradation began to occur. Analyses and i.r. spectral data of the product from $SiMe_3(SEt)$ + WCl_6 suggested that loss of EtCl was occurring: [$WCl_5(SEt)$] $\longrightarrow$ [$WSCl_4$] + EtCl. The presence of a band at 560 cm^{-1} [ν(W=S)] in the i.r. spectra of these products suggested that they were contaminated with $WSCl_4$. The mode of degradation was confirmed by isolation of EtCl as the major volatile liquid product from thermal decomposition of the crude [$WCl_5(SEt)$] in an evacuated sealed tube. In this same experiment, solid $WSCl_4$ also sublimed out.

Thermal Decomposition Studies.—In view of these observations on the decomposition of [$WCl_5(SEt)$], a systematic survey of the thermal decomposition of the [$WCl_5(SR)$] products was carried out. The identity of the volatile products was established from their n.m.r. spectra (Table 1). Two possible products occur, alkyl chlorides and dialkyl disulphides. The ^1H n.m.r. spectrum of the volatiles from the cyclohexane thiolato-species was complex, and a g.c.–mass spectral study was required. This study showed that in addition to chlorocyclohexane and dicyclohexyl disulphide a major component of the decomposition volatiles is 1-chloro-1-methylcyclopentane. Minor amounts of three isomers of dichlorocyclohexane were also identified. The significance of this diverse collection of products is that it implies that degradation reactions other than elimination of RCl can occur at these higher temperatures. This conclusion is also supported by the nature of the solid residues which are produced in addition to $\mathrm{WSCl_4}$. Dark brown materials, produced in all these reactions, were extremely unreactive and had a high tungsten content. Some variation in the latter content was observed, suggesting an ill defined phase which was not further investigated.

TABLE 1

Hydrogen-1 n.m.r. data for volatiles from the thermal decomposition reactions

R	δ/p.p.m.	Ratio *	Assignment
Ph	7.35 (s)	1.0	$\mathrm{(C_6\mathit{H}_5S)_2}$
Me	2.44 (s)	1.2	$\mathrm{C\mathit{H}_3SSC\mathit{H}_3}$
	3.03 (s)	1.0	$\mathrm{C\mathit{H}_3Cl}$
Et	1.45 (m)		$\mathrm{(C\mathit{H}_3CH_2S)_2}$ and $\mathrm{C\mathit{H}_3CH_2Cl}$
	2.70 (q)	2.0	$\mathrm{CH_3C\mathit{H}_2SSC\mathit{H}_2CH_3}$
	3.56	1.0	$\mathrm{CH_3C\mathit{H}_2Cl}$
$\mathrm{Bu^i}$	1.01 (m)	3.5	$\mathrm{[(C\mathit{H}_3)_2CHCH_2S]_2}$ and/or $\mathrm{(CH_3)_3CSSCH_2CH(C\mathit{H}_3)_2}$
	1.35 (s)	1.0	$\mathrm{[(C\mathit{H}_3)_3CS]_2}$ and/or $\mathrm{(C\mathit{H}_3)_3CSSCH_2CH(CH_3)_2}$
	1.70 (s)	6.7	$\mathrm{(C\mathit{H}_3)_3CCl}$
	2.41 (d)	1.0	$\mathrm{[(CH_3)_2CHC\mathit{H}_2S]_2}$ and/or $\mathrm{(CH_3)_3CSSC\mathit{H}_2CH(CH_3)_2}$
$\mathrm{Bu^t}$	1.38 (s)	1.0	$\mathrm{(C\mathit{H}_3)_3CSSC(C\mathit{H}_3)_3}$
	1.70 (s)	5.0	$\mathrm{(C\mathit{H}_3)_3CCl}$
$\mathrm{CH_2Ph}$	4.58	1.0	$\mathrm{ClC\mathit{H}_2C_6H_5}$
	7.38		$\mathrm{ClCH_2C_6\mathit{H}_5}$

* Approximate molar ratio based on peak areas.

Although the above thermal studies were successful in confirming the loss of RCl as a major pathway to decomposition, the relatively high temperature employed might well have contributed to the adoption of higher energy pathways, such as reductive elimination of sulphenyl chlorides, RSCl. Such species are themselves unstable [9] and would be capable of yielding small quantities of other products.

Solution Decomposition Studies.—In view of the complex nature of some of the above reactions the more direct approach of studying the ^{1}H n.m.r. spectra of reaction solutions was adopted. It proved to be a very sensitive method of establishing relative kinetic stabilities of the $\mathrm{[WCl_5(SR)]}$ species, and of probing possible mechanisms.

The 1 : 1 reactions between $\mathrm{WCl_6}$ and $\mathrm{SiMe_3(SR)}$ were carried out in $\mathrm{CS_2}$ solutions, and ^{1}H n.m.r. spectra run periodically over the course of 12 h. The data in Table 2 show the products identified from the ^{1}H n.m.r. spectra of solutions for a range of R groups. The chemical shifts were always subject to displacement from their normal values in $\mathrm{CS_2}$ due to the presence of small amounts of paramagnetic species, and hence all decomposition products were identified by standard addition. Many of the solutions eventually deposited black solids, similar in nature to the residues from the thermal decomposition studies.

The important results from this study are as follows. (*i*) Immediate and quantitative reaction of $\mathrm{SiMe_3(SR)}$ with $\mathrm{WCl_6}$ occurred. The n.m.r. signal of $\mathrm{SiMe_3(SR)}$ was always replaced by that of $\mathrm{SiMe_3Cl}$. (*ii*) The signal due to $\mathrm{[WCl_5(SR)]}$ could be identified in most cases in very freshly prepared solutions. This signal diminished with time, and for some cases could not be observed at all. (*iii*) The intensities of signals due to RCl and/or $\mathrm{R_2S_2}$ increased with time but their ratio varied from one R group to another. (*iv*) $\mathrm{WSCl_4}$ was identified as a component of most reactions upon evaporation of some of the solvent. It was not found in the case of R = Ph, in which no PhCl was observed.

TABLE 2

Hydrogen-1 n.m.r. data for solution reactions

R	δ	Ratio [a]	Assignment
Ph	7.61	1.0	$\mathrm{[WCl_5(SC_6\mathit{H}_5)]}$
	8.10	1.0	$\mathrm{C_6\mathit{H}_5SSC_6\mathit{H}_5}$
	0.57s		$\mathrm{(CH_3)_3SiCl}$
Me	2.28s	3.0	$\mathrm{[WCl_5(SC\mathit{H}_3)]}$
	2.60s	3.0	$\mathrm{C\mathit{H}_3SSC\mathit{H}_3}$
	3.36s	1.0	$\mathrm{C\mathit{H}_3Cl}$
	0.57s		$\mathrm{(C\mathit{H}_3)_3SiCl}$
Et [b]	1.40m		
	2.45m		
	0.57s		$\mathrm{(C\mathit{H}_3)_3SiCl}$
cyclo-$\mathrm{C_6H_{11}}$	1.4s		$\mathrm{C\mathit{H}_3}$-cyclo-$\mathrm{C_5H_8Cl}$
	1.61		
	1.72		
	2.03		
	0.55		$\mathrm{(C\mathit{H}_3)_3SiCl}$
$\mathrm{Bu^i}$	1.30	3.0	$\mathrm{[(C\mathit{H}_3)_2CHCH_2S]_2}$
	2.37		$\mathrm{[(CH_3)_2CHC\mathit{H}_2S]_2}$
	1.60	1.0	$\mathrm{(C\mathit{H}_3)_3CCl}$
	0.78		$\mathrm{(C\mathit{H}_3)_3SiCl}$
$\mathrm{Bu^t}$	1.35	1.0	$\mathrm{[(C\mathit{H}_3)_3CS]_2}$
	1.70	4.0	$\mathrm{(C\mathit{H}_3)_3CCl}$
	0.53		$\mathrm{(C\mathit{H}_3)_3SiCl}$
$\mathrm{CH_2Ph}$	3.64	1.0 [c]	$\mathrm{[WCl_5(SC\mathit{H}_2C_6H_5)]}$
	3.91	2.0	$\mathrm{(SC\mathit{H}_2C_6H_5)_2}$
	4.52	7.0	$\mathrm{ClC\mathit{H}_2C_6H_5}$
	7.18		$\mathrm{[WCl_5(SCH_2C_6\mathit{H}_5)]}$
	7.29		$\mathrm{(SCH_2C_6\mathit{H}_5)_2}$
	7.33		$\mathrm{ClCH_2C_6\mathit{H}_5}$
	0.62		$\mathrm{(C\mathit{H}_3)_3SiCl}$

[a] Approximate molar ratio based on peak areas *ca.* 0.5 h after mixing of reagents. [b] Ethyl case did not give a first-order spectrum. [c] Not seen after *ca.* 3 h.

DISCUSSION

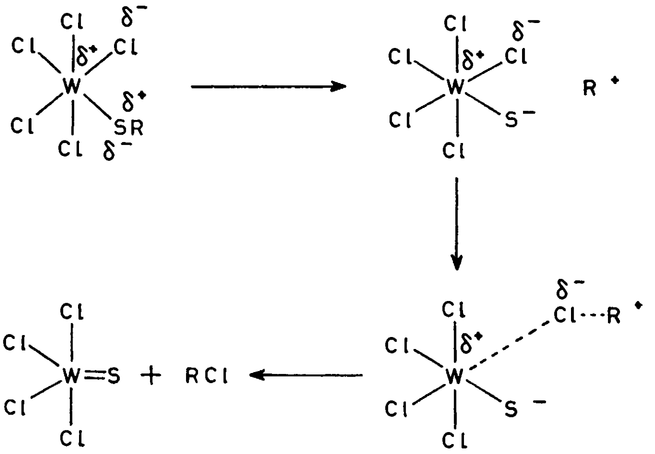
Comparison of the data in Tables 1 and 2 shows that most of the products identified in the decomposition of each $\mathrm{[WCl_5(SR)]}$ compound are common to both the thermal and room-temperature solution degradations. This is summarized in Table 3. The obvious conclusion is that with the exception of minor side reactions the two major pathways are the same. One of these involves elimination of $\mathrm{R_2S_2}$ while the other yields alkyl chloride. The relative importance of each is a function of the R groups.

TABLE 3

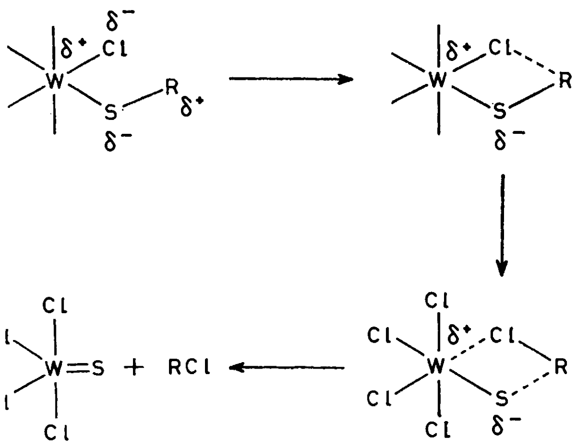
Summary of decomposition products identified

R	Products
Ph	$\mathrm{WSCl_4}$, $\mathrm{(PhS)_2}$
Me	$\mathrm{WSCl_4}$, $\mathrm{(MeS)_2}$, MeCl
Et	$\mathrm{WSCl_4}$, $\mathrm{(EtS)_2}$, EtCl
cyclo-$\mathrm{C_6H_{11}}$	$\mathrm{WSCl_4}$, $\mathrm{(C_6H_{11}S)_2}$, $\mathrm{C_5H_8CH_3Cl}$, $\mathrm{C_6H_{11}Cl}$, $\mathrm{C_6H_{10}Cl_2}$
$\mathrm{Bu^i}$	$\mathrm{WSCl_4}$, $\mathrm{(Bu^iS)_2}$, $\mathrm{(Bu^tS)_2}$ or $\mathrm{Bu^tSSBu^i}$, $\mathrm{Bu^tCl}$
$\mathrm{Bu^t}$	$\mathrm{WSCl_4}$, $\mathrm{(Bu^tS)_2}$, $\mathrm{Bu^tCl}$
$\mathrm{CH_2Ph}$	$\mathrm{WSCl_4}$, $\mathrm{(PhCH_2S)_2}$, $\mathrm{PhCH_2Cl}$

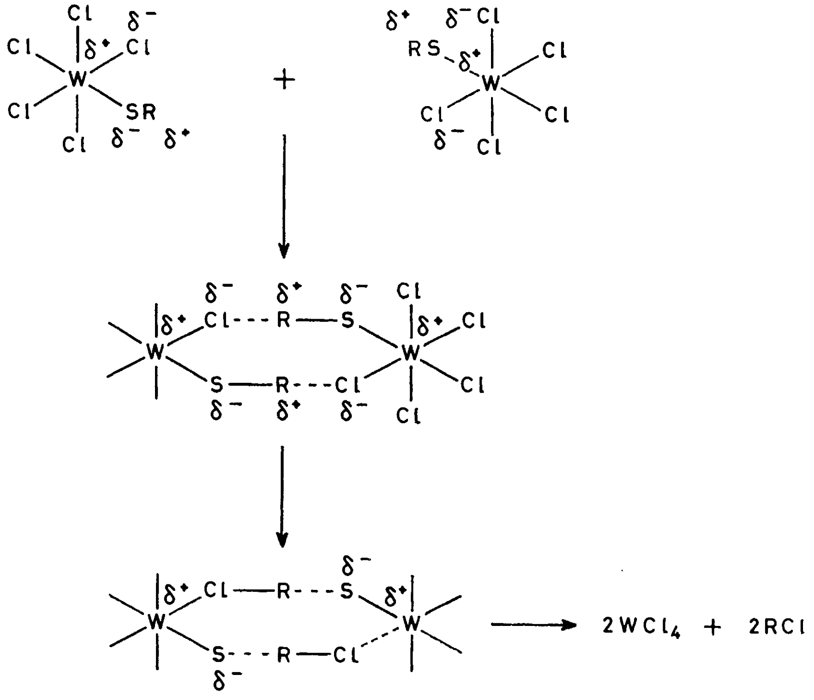
Elimination of Alkyl Chloride.—Four possible mechanisms could occur by which RCl could be produced. These will be considered and the evidence examined to deduce which is most likely. (1) Reductive elimination of RSCl followed by its decomposition [9] to RCl and other products. (2) Dissociative intramolecular reaction * (Scheme 1). (3) Nucleophilic intramolecular reaction (Scheme 2). (4) Associative intermolecular reaction (Scheme 3). Mechanism (1), in which RSCl would be the initial product, cannot be supported by the solution data. In no case was RSCl observed, and in any event the tungsten product expected would be WCl_4, rather than $WSCl_4$. In every case where RCl was observed, so also was $WSCl_4$. It is therefore more probable that RCl is a direct reaction product.



Scheme 1



Scheme 2



Scheme 3

The kinetic stability of [$WCl_5(SR)$] will now be examined in the light of the three most likely mechanisms, (2)—(4). The dissociative mechanism would proceed on the basis of the stability of R^+, since the more stable the carbonium ion the more energetically favourable is the dissociation.[10] Both of the nucleophilic processes (3) and (4) would be favoured by factors enhancing S_N2 reactions, and more importantly here would be hindered by branching at the α and β carbon atoms. Thus tertiary carbon atoms should strongly resist such attack. The observed stability sequence with respect to generation of RCl by [$WCl_5(SR)$] is: $Ph > Me > Et \sim cyclo\text{-}C_6H_{11} \approx Bu^i > Bu^t \approx CH_2Ph$.

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* A referee has suggested that abstraction of Cl^- from a second molecule of [$WCl_5(SR)$] might be possible. We consider this less likely than the intramolecular reaction shown here, on the basis of the tungsten products identified.

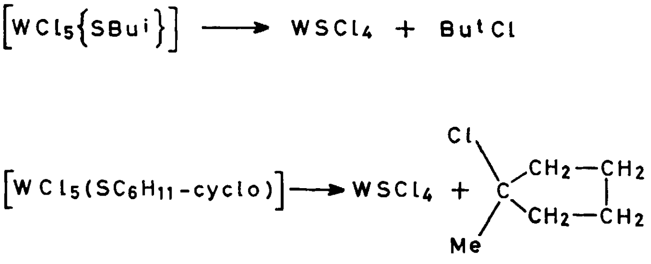
Table 4 shows the predicted kinetic stabilities for the three mechanisms. Clearly the most likely is that involving the formation of a carbonium ion (2). This conclusion is further supported by the following evidence. The selection of R = isobutyl or cyclohexyl allows a check to be made for carbonium-ion rearrangements. Both $\mathrm{Me_2CHCH_2^+}$ and cyclo-$\mathrm{C_6H_{11}^+}$ are known to rearrange[10] to the more stable ions, namely t-butyl and methylcyclopentyl carbonium ions respectively. In both of these cases products due to such rearrangements were observed (Scheme 4). In the case of $[\mathrm{WCl_5(SPh)}]$, no PhCl was identified as a degradation product. This is to be expected since the phenyl carbonium ion is noted[10] for its instability, thus precluding this mechanism of decomposition.

TABLE 4

Predicted stabilities of $[\mathrm{WCl_5(SR)}]$ on basis of reaction mechanism

Mechanism	(2)	(3)	(4)
Most stable	Ph	$\mathrm{Bu^t}$	$\mathrm{Bu^t}$
	Me	Ph	Ph
	Et	$\mathrm{Bu^i}$	$\mathrm{Bu^i}$
	cyclo-$\mathrm{C_6H_{11}}$	cyclo-$\mathrm{C_6H_{11}}$	cyclo-$\mathrm{C_6H_{11}}$
	$\mathrm{Bu^i}$	Et	Et
	$\mathrm{Bu^t}$	Me	Me
	$\mathrm{CH_2Ph}$	$\mathrm{CH_2Ph}$	$\mathrm{CH_2Ph}$
Least stable			

We carried out several experiments to test the reversibility of these reactions. These involved either sealed-tube or $\mathrm{CS_2}$ solution reactions between selected RCl species and $\mathrm{WSCl_4}$. Not surprisingly, in view of the obvious thermodynamic as well as kinetic instability of the $[\mathrm{WCl_5(SR)}]$ species, no products of this formula could be isolated. However in sealed-tube reactions between $\mathrm{WSCl_4}$ and isobutyl chloride or cyclohexyl chloride evidence for the formation of carbonium ions was observed. Upon analyzing the RCl solvents after the reactions, rearranged products (t-butyl chloride and 1-methyl-1-chlorocyclopentane) were found to have been generated. In addition, small quantities of disulphides were present which must have arisen from the alternative decomposition pathway of $[\mathrm{WCl_5(SR)}]$. No evidence for reaction was observed in the control experiments in which RCl was heated to 150 °C in the absence of $\mathrm{WSCl_4}$. At lower temperatures, refluxing of $\mathrm{WSCl_4}$ in RCl at *ca.* 60 °C, there was no evidence for any reaction between these reagents.



SCHEME 4

Elimination of $\mathrm{R_2S_2}$.—As shown in Tables 1 and 2 the elimination of $\mathrm{R_2S_2}$ is a competitive mode of decomposition of $[\mathrm{WCl_5(SR)}]$ with loss of RCl. As the stability of $\mathrm{R^+}$ decreases, the importance of reductive elimination of $\mathrm{R_2S_2}$ is enhanced. Although the intramolecular elimination of $\mathrm{R_2S_2}$ from systems with more than one SR ligand is well known,[6] it is clear that an intermolecular mechanism must occur in the present case. The obvious bimolecular reaction (2) is probably too simplistic to

$$\mathrm{Cl_5W{-}SR + RS{-}WCl_5 \longrightarrow R_2S_2 + W_2Cl_{10}} \qquad (2)$$

account for the intractable solid residues which form. Furthermore no evidence was found for production of $\mathrm{W_2Cl_{10}}$. This compound may be formed as an intermediate which reacts further with either starting compound or $\mathrm{WSCl_4}$, eventually leading to oligomeric products. No further investigations on this aspect of the degradation were carried out.

Conclusions.—The degradation of $[\mathrm{WCl_5(SR)}]$ is a kinetically controlled process. Two major pathways have been found, the most significant of which is the elimination of RCl *via* a carbonium-ion mechanism. Although to our knowledge no direct evidence has been reported previously to suggest that a metal ion is capable of activating a C–S bond to the extent that heterolytic cleavage occurs, a number of published observations would be compatible with such a mechanism. For example it is reported by Satchell[11] that reaction (3) occurs. A plausible explanation would be that initially

$$[\mathrm{Hg(SBu^t)_2}] \xrightarrow{\text{Heat}} \mathrm{Bu^tSH + Me_2C{=}CH_2 + HgS} \qquad (3)$$

$\mathrm{Me_3C^+}$ is liberated which could eliminate a proton[10] to yield the alkene. The proton would attack a further co-ordinated $\mathrm{Bu^tS}$ group to yield the thiol. The direct observation of a carbonium-ion mechanism under mild conditions reported here is of possible relevance to biological methylation reactions. Certain of these reactions have been shown to be capable of utilizing methionine as a source of methyl. The possibility of metal activation of this molecule to release $\mathrm{CH_3^+}$ is suggested by the results described here.

Several reports of *S*-dealkylation of co-ordinated thioethers have appeared in the literature.[12] Usually the eliminated alkyl group is isolated as an alkyl chloride, but in one case reported from this laboratory, as a sulphonium ion.[13] Studies of $[\mathrm{WX_5(OMe)}]$, (X = Cl or F) showed that these two compounds are also unstable to loss of MeX with concomitant production of $\mathrm{WOX_4}$, although no mechanism was suggested.[14]

We are continuing our study of the reactions of co-ordinated thiolate ions in an attempt to establish the generality of carbonium-ion release.

EXPERIMENTAL

All handling procedures were carried out under an inert atmosphere. Tungsten hexachloride (Alfa Inorganics) was twice resublimed *in vacuo* before use. Solvents were dried, degassed, and distilled by the usual methods. Analyses for W and Cl were carried out in these laboratories as previously described.[15] Other elemental analyses were obtained commercially from Alfred Bernhardt Laboratories. Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer 467 spectrophotometer. Hydrogen-1 n.m.r. spectra were routinely determined using a Hitachi–Perkin-Elmer R-24B spectrometer without a lock, but important spectra were run either on a Bruker WH90 F-T or on a Varian HA100 n.m.r. spectrometer, both with external locks. Product analysis by g.c.–m.s. utilized a Hewlett–Packard 5992-A system.

Synthesis.—Preparation of alkylthiotrimethylsilane reagents was accomplished by the literature methods.[16] Reactions with WCl$_6$ were very sensitive to stoicheiometry, so that this was rigorously controlled at 1 : 1. Typically WCl$_6$ (1 g) was dissolved in CS$_2$ (*ca.* 150 cm^3) and to this solution was added the calculated amount of the silyl reagent solution made up in the same solvent (2 g in 25 cm^3). The flask was then stoppered and the solution stirred for 15—20 min. An n.m.r. sample was then removed and a spectrum run. The bulk solution was then reduced in volume until a precipitate began to form, which was filtered off, washed with hexane, and dried *in vacuo*. Yields were typically 60—70%, based on WCl$_6$. If necessary the solvent was completely removed to produce a solid product. The possibility of CS$_2$ interfering with the synthesis by insertion into the W–S bond was checked by carrying out selected syntheses in CH$_2$Cl$_2$ as well as in CS$_2$. The products were found to be the same from both solvents. Analytical data for pure [WCl$_5$(SR)] compounds are given in Table 5. The i.r. spectra of [WCl$_5$(SMe)] contains two very strong bands at 320 and 370 cm^{-1} characteristic of W–Cl stretching modes, and a weak band at 450 cm^{-1} probably due to a W–S vibration. Other peaks characteristic of co-ordinated SMe are observed in regions 950—990 cm^{-1} (CH$_3$ rocking) and 1 290—1 315 cm^{-1} (CH$_3$ sym bend). The benzenethiolate analogue also shows ν(W–Cl) bands at 320 and 370 cm^{-1} and a band at 478 cm^{-1} probably due to ν(W–S). Bands associated with the phenyl ring occur in the region 1 062—1 177 cm^{-1}. Both spectra were devoid of any peak assignable to a terminal ν(W=S). However, for all other R groups studied even the best samples showed bands in the *ca.* 570 cm^{-1} region indicative of the presence of WSCl$_4$ [literature value ν(W=S) at 569 cm^{-1}].[17] The relative intensity of ν(W=S) increased from R = Et and Bu^i to R = Bu^t and CH$_2$Ph as expected from the arguments relating to carbonium-ion stability. Analytical data for the species obtained for R = Bu^t, CH$_2$Ph were fully consistent with the products of reaction being mixtures of WSCl$_4$ and [WCl$_5$(SR)]. {R = Bu^t. Found: W, 49.1. [WCl$_5$(SBu^t)] requires W, 40.85. WSCl$_4$ requires W, 51.4. R = CH$_2$Ph. Found: W, 48.1. [WCl$_5$(SCH$_2$Ph)] requires W, 38.0%}. Traces of other degradation products resulting from the loss of R$_2$S$_2$ would also be present. No further attempts were made to isolate pure products for the full range of R groups in view of the demonstrated instability of most of the compounds in solution.

TABLE 5

Analytical data (%) for [WCl$_5$(SR)] products (calculated values in parentheses)

Compound	W	Cl	C	H	S
[WCl$_5$(SMe)]	45.7	43.9	3.15	0.60	8.05
	(45.1)	(43.4)	(2.95)	(0.75)	(7.85)
[WCl$_5$(SPh)]	39.5	37.5	15.6	1.20	6.70
	(39.1)	(37.7)	(15.3)	(1.05)	(6.80)

Thermal decomposition of the isolated solids was effected by heating 30 mg samples in an evacuated sealed tube for 3 h at 200 °C. Volatiles were collected in a side arm, cooled by liquid nitrogen. Some CS$_2$ (*ca.* 1 cm^3) was also sealed into the side arms, so that upon warming to room temperature sufficient quantities of highly volatile species could be retained in solution for the n.m.r. spectrum. In selected cases the volatiles were collected without a solvent and analyzed by g.c.–m.s.

Reaction of WSCl$_4$ *and* RCl.—The sealed-tube reactions were carried out between *ca.* 0.05 g of WSCl$_4$ and *ca.* 1 cm^3 of the appropriate alkyl or aryl chloride. The main body of the tube was heated to 150 °C in a furnace, and after 20 min the liquids were trapped into a side arm, which was then sealed. The residual solid was examined by i.r. spectroscopy, which showed it to be WSCl$_4$ in every case. The liquid was examined by ^{1}H n.m.r. spectroscopy, and products identified as described earlier.

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