Oxotrichlororhenium(v), $ReOCl_3$

By P. W. FRAIS and C. J. L. LOCK*
(*Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada*)
and A. GUEST
(*Department of Chemistry, University of the West Indies, Mona, Jamaica*)

Summary The preparation of $ReOCl_3$, by photodecomposition of $ReOCl_4$ and other methods, is described.

FOLLOWING the preparation of the first complexes of $ReOCl_3$,[1] many reports of further complexes appeared,[2] but so far there has been no report of the successful preparation of $ReOCl_3$. Edwards *et al.*[3] recently reported a number of methods which were used in attempts to prepare $ReOCl_3$, but which were unsuccessful. We have independently used these same methods, also with no success, but we have found three methods for the successful preparation of $ReOCl_3$. We have also shown that $ReOCl_3$ exists in at least two different solid forms.

The first two methods of preparation involve the reaction of $ReCl_5$ with ReO_3 or $ReCl_5$ with ReO_2 at 300° in sealed tubes. These reactions are not clean; depending on the ratio of the reactants varying amounts of ReO_3Cl, $ReOCl_4$, Re_3Cl_9, and even rhenium metal are produced, and $ReOCl_3$ is rarely the major product. However, it is possible to separate $ReOCl_3$ from the other products by careful trap to trap distillation *in vacuo*, and most of our work has been done on $ReOCl_3$ produced by these methods.

More recently we have discovered a third, and far more satisfactory way of producing $ReOCl_3$ by the photodecomposition of $ReOCl_4$ using 3500 Å light. Yields of greater than 50% can be obtained by irradiating 1 g of $ReOCl_4$ for 12 h in a Rayonet Photochemical Reactor with 16 RPR 3500 Å lamps.

X-Ray powder data for α- and β-$ReOCl_3$

α-$ReOCl_3$		β-$ReOCl_3$	
d (Å)	*I*	*d* (Å)	*I*
5·90	65	5·95	66
5·60	94	4·81	23
5·22	55	4·42	47
4·52	100	4·28	71
4·34	44	4·11	<4
4·21	8	4·01	13
3·89	<6	3·88	39
3·69	<6	3·80	12
3·59	52	3·68	6
3·51	70	3·60	<5
3·36	10	3·50	<5
3·21	10	3·36	<5
3·13	58	3·17	33
2·97	13 (broad)	3·09	100
2·87	10	3·03	<5
2·77	13	2·98	<5
2·68	42	2·82	<5
2·61	72	2·75	39
2·55	<6	2·69	17
2·51	14	2·60	9
2·48	37	2·56 }	
21 others		2·53 }	*ca.* 14 (broad)
		18 others	

Cu-K_α radiation. Microdensitometer intensities.

$ReOCl_3$ was usually obtained at room temperatures as purple frost-like plates and we designate this form α-$ReOCl_3$. It was difficult to obtain a good i.r. spectrum of this material as it decomposed very rapidly to other oxochlorides during the preparation of the i.r. sample. However, a peak was always observed in the i.r. spectrum at 1018 cm^{-1} and in some samples this was the only peak in the 850—1050 cm^{-1} region; we assign this to a terminal Re=O stretch of α-$ReOCl_3$. Analyses for Re and Cl and determination of the oxidation state of Re by neutron activation[4] were consistent with the $ReOCl_3$ formulation. The powder pattern of a sample of α-$ReOCl_3$ (Table) showed a superficial resemblance to that of monoclinic $MoOCl_3$,[5] but a detailed examination suggests that the two compounds are not isomorphous.

On standing *in vacuo*, the purple "frost" forms thin dichroic purple grey, plate-like crystals by vapour-phase transport. This second form of $ReOCl_3$ (designated β-$ReOCl_3$) has a powder diffraction pattern quite different from that of α-$ReOCl_3$ (see Table). A single-crystal *X*-ray study shows that the compound is triclinic with $a = 6{\cdot}10$ $b = 12{\cdot}98$, $c = 6{\cdot}05$ Å, $\alpha = 88{\cdot}4°$, $\beta = 95{\cdot}4°$, $\gamma = 105{\cdot}6°$ and $Z = 4$. The volume of the unit cell is 459·1 Å^3, which is very close to that of $MoOCl_3$.[5] The unit-cell parameters appear to be related to those of monoclinic $MoOCl_3$. However, a comparison of the intensities of the individual reflections as well as a comparison of the powder diffraction patterns show clearly that the structures must be quite different.

The i.r. spectrum shows a peak at 1018 cm^{-1}, which we assign to a terminal Re=O stretch.

β-$ReOCl_3$ appears to be more stable than α-$ReOCl_3$, and melts at 78° with only minor decomposition. At higher temperatures, *in vacuo*, and on dissolution in CCl_4 or $TiCl_4$ both forms of $ReOCl_3$ decompose readily to yield $ReOCl_4$, Re_3Cl_9, and ReO_3Cl in a reaction such as

$$5ReOCl_3 \rightarrow \tfrac{2}{3}Re_3Cl_9 + 2ReOCl_4 + ReO_3Cl$$

However, at room temperature *in vacuo*, α-$ReOCl_3$ can be sublimed into a liquid-nitrogen-cooled trap, yielding a pale straw-yellow solid, which decomposes above −40° to give α-$ReOCl_3$. The yellow solid can be trap-to-trap distilled at temperatures below −40°. Analysis has shown that the Re : Cl atom ratio is 1 : 3 and in view of its ready re-conversion into α-$ReOCl_3$, the material may be the $ReOCl_3$ monomer. The instability and small quantities which we have obtained so far have precluded further physical examination.

(*Received, November 16th, 1970; Com. 1978.*)

[1] C. J. L. Lock and G. Wilkinson, *Chem. and Ind.*, **1962**, **40**.
[2] N. P. Johnson, C. J. L. Lock, and G. Wilkinson, *J. Chem. Soc.*, **1964**, 1054; J. Chatt and G. A. Rowe, *ibid.*, **1962**, 4019; J. E. Fergusson, *Coord. Chem. Rev.*, **1966**, **1**, 459, and references therein.
[3] D. A. Edwards and R. T. Ward, *J. Chem. Soc.* (*A*), **1970**, 1617.
[4] W. D. Courrier, A. Guest, C. J. L. Lock, and R. H. Tomlinson, *Canad. J. Chem.*, **1968**, **46**, 2965.
[5] M. G. B. Drew and I. B. Tomkins, *J. Chem. Soc.* (*A*), **1970**, 22.