

## Preparation of Oxotetrachlororhenates (V) from $H_2ReOCl_5$ in Acetic Acid

V YATIRAJAM\* & (Miss) M LAKSHMI KANTAM

Department of Chemistry, Kurukshetra University, Kurukshetra  
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Olive-green crystalline salts,  $Ph_4AsReOCl_4$  and  $Ph_4PReOCl_4$ , have been prepared in good yields starting from  $H_2ReOCl_5$ . Yellow coloured concentrate of  $H_2ReOCl_5$  has been prepared by extraction of  $ReOCl_3^-$  into methyl ethyl ketone and its transfer into acetic acid.

The only method reported<sup>1</sup> for the preparation of oxotetrachlororhenate(V) anion,  $ReOCl_4^-$ , is by reduction of perrhenate with zinc in a reaction mixture containing methanol, sulphuric acid and hydrochloric acid. The adjustment of the conditions was fortuitous. Only tetraphenylarsonium salt of the anion  $ReOCl_4^-$  was reported with an yield of only 13%. We report here a new method for the preparation of  $ReOCl_4^-$  anion using  $H_2ReOCl_5$  in anhydrous acetic acid, the  $H_2ReOCl_5$  being obtained from  $KReO_4$  by solvent extraction. The arsonium and phosphonium salts of the  $ReOCl_4^-$  anion have been also obtained in good yields.

Petroleum ether (60-80°) and other solvents and chemicals were of high purity and were dried thoroughly. Experiments were carried out in a glove box under dry nitrogen. Acetic acid-HCl mixture was prepared by saturating anhydrous acetic acid with dry hydrogen chloride gas.

### Preparation of green Re(V) species

Yellow coloured concentrate (8 ml; 113 mg Re) of  $H_2ReOCl_5$  in acetic acid, prepared as reported earlier<sup>2</sup>, was shaken with pet. ether (10 ml). The yellow layer was separated and shaken well with acetic anhydride (3.6 ml) when the solution turned green. This was then shaken with pet ether (20 ml) and the lower layer was separated. The latter contains the green Re(V) species in high concentration.

### Preparation of oxotetrachlororhenates(V)

The yellow viscous concentrate obtained<sup>2</sup> from 0.350 g of  $KReO_4$  was dissolved in acetic acid-HCl (30 ml). To this was added tetraphenylarsonium chloride (1.057 g) in acetic acid-HCl (15 ml). On vigorous shaking, a crystalline olive-green precipitate was formed. After decanting off the supernatant liquid, the precipitate was washed with acetic acid-HCl, finally with petroleum ether and dried under nitrogen; yield, 0.53 g (60%).

$Ph_4PReOCl_4$  was prepared in the same way as the arsonium salt, taking 0.250 g of  $KReO_4$  and 0.650 g of tetraphenylphosphonium chloride; yield, 0.44 g (75%).

Both the compounds are soluble in dichloromethane, acetone, ethanol, acetonitrile and nitromethane.

Spectra were recorded on Beckman DU-2, Beckman IR-20 and Brucker IFS-113 spectrophotometers. Magnetic susceptibilities were determined by the Gouy method and conductivities were measured in nitromethane on a Philips bridge, PR 9500/90. After peroxide decomposition of the complexes, rhenium<sup>3</sup> was determined as  $Ph_4AsReO_4$  and chloride<sup>4</sup> as  $AgCl$ .

Table 1—Analytical and Physical Data of Oxotetrachlororhenates(V)

Compound	Found (Calc, %)				$\mu_{eff}^*$	Electronic spectra† nm( $\epsilon$ )
	Re	Cl	C	H		
$Ph_4AsReOCl_4$	24.50 (25.58)	19.51 (19.56)	39.75 (39.61)	2.65 (2.75)	0.75	240 430(28) 490(26) 830(17) 1180(18)
$Ph_4PReOCl_4$	26.35 (27.23)	20.58 (20.79)	42.03 (42.16)	2.83 (2.92)	0.57	240 430(33) 490(30) 830(21) 1180(22)

\* at 18 C, † in acetonitrile

The yellow concentrate of  $\text{H}_2\text{ReOCl}_5$  in acetic acid shows the same electronic spectrum<sup>5</sup> of  $\text{ReOCl}_5^{2-}$  as is shown in conc. HCl. Acetic anhydride abstracts HCl from  $\text{H}_2\text{ReOCl}_5$  producing the green species  $\text{HReOCl}_4$ , which shows the same electronic spectrum as that shown by oxotetrachlororhenates(V) (vide infra). Most of the acetic acid and acetic anhydride pass into the light pet. ether and the green species gets concentrated in the lower layer.

#### *Oxotetrachlororhenates(V)*

The analytical and physical data of the salts are given in Table 1. The salts are olive-green in colour and analyse satisfactorily to  $\text{Ph}_4\text{AsReOCl}_4$  and  $\text{Ph}_4\text{PReOCl}_4$ . Their molar conductivities in nitromethane (69 and 72  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ ) show that they are 1:1 electrolytes<sup>6</sup>; their  $\mu_{\text{eff}}$  values are as expected for Re(V) ion.

The electronic spectral data of  $\text{Ph}_4\text{AsReOCl}_4$  and  $\text{Ph}_4\text{PReOCl}_4$  are given in Table 1. In the IR spectra,  $\nu(\text{ReO})$ , observed at 1038 and 1035  $\text{cm}^{-1}$  respectively, is comparable to the value shown by  $\text{ReOCl}_4^-$  (1033  $\text{cm}^{-1}$ )<sup>7,8</sup> and by  $\text{ReOBr}_4^-$  (1035  $\text{cm}^{-1}$ )<sup>1</sup>.

The complexes turn yellow on standing for several days in the mother liquor. The yellow salts obtained on keeping the two olive-green salts in mother liquor do not show the IR bands at 1038 and 1035  $\text{cm}^{-1}$ . Instead, a strong band at 998  $\text{cm}^{-1}$  is observed which overlaps with that of the reagent at the same position. Infrared spectra of the olive-green salts in KBr show weaker bands at 1038 and 1035  $\text{cm}^{-1}$  respectively and a stronger band at 998  $\text{cm}^{-1}$ . These changes in the spectra indicate that the  $\text{ReOCl}_4^-$  ion of the green salts is probably converted to  $\text{ReOCl}_5^{2-}$  and  $\text{ReOCl}_4\text{Br}^{2-}$  respectively. Such lowering of  $\nu(\text{ReO})$  frequency is shown when rhenium changes its coordination number from five to six with a ligand *trans* to oxygen —  $\text{ReOCl}_4$

shows  $\nu(\text{ReO})$  at 1033  $\text{cm}^{-1}$  while  $\text{ReOCl}_4(\text{OH}_2)$  and  $\text{ReOCl}_4\cdot\text{OPCl}_3$  show the band at 1016 and 1020  $\text{cm}^{-1}$  respectively<sup>8</sup>. Similarly,  $\text{ReOBr}_4^-$  shows  $\nu(\text{ReO})$  at 1035  $\text{cm}^{-1}$  whereas  $\text{ReOBr}_4(\text{OH}_2)^-$  shows<sup>9</sup> it at 1000  $\pm 5\text{ cm}^{-1}$ . Hence, the above observations confirm that the rhenium in the green anion is five-coordinated.

The  $\text{Ph}_4\text{AsReOCl}_4$  salt reported earlier<sup>1</sup> was a cream-coloured powder and was immediately converted to the acetonitrile adduct. It showed  $\nu(\text{ReO})$  at 1000  $\pm 5\text{ cm}^{-1}$  and not at 1038  $\text{cm}^{-1}$  as observed in the present work. Hence, that compound might be  $\text{Ph}_4\text{AsReOCl}_4(\text{OH}_2)$  or highly contaminated with it, as it was precipitated from an aqueous medium and no special precautions seem to have been taken to exclude moisture during handling.

The far IR spectrum of  $\text{Ph}_4\text{PReOCl}_4$  shows bands ( $\text{cm}^{-1}$ ) at 333.6(s), 239.2(m), 353.2(m), 291.6(w) and 164.4(w). They may be assigned as  $\nu_2$ ,  $\nu_3$ ,  $\nu_7$ ,  $\nu_8$  and  $\nu_9$  modes of  $\text{ReOCl}_4^-$  ion respectively on the basis of analogy with the stretching frequencies in  $\text{MoOCl}_4^-$  ion<sup>10</sup>.

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