289. *Ethoxides and* iso*Propoxides of Manganese and Rhenium.*

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Manganese and rhenium ethoxides and *iso*propoxides, $Mn(OR)_2$ and $Re(OR)_3$, have been prepared by the interaction of the chlorides of the elements with sodium ethoxide and *iso*propoxide. The products are only stable in dry air, since water very readily hydrolyses them.

Compounds of the halides of manganese and rhenium with one molecule of ethyl or *iso*propyl alcohol have also been obtained.

NEITHER manganese nor rhenium dissolves in or reacts with methyl, ethyl, or *iso*propyl alcohol to give an alkoxide, but the ethoxides and iso*propoxides* of both metals have been obtained by the interaction of dry alcoholic solutions of their halides with the appropriate sodium alkoxide, *e.g.*, $ReCl_3 + 3NaOEt = 3NaCl + Re(OEt)_3$. Manganese ethoxide, $Mn(OC_2H_5)_2$, has already been made (Kandelaky, Setaschwili, and Tawberidge, *Kolloid-Z.*, 1935, **73**, 47), but the other compounds have not previously been described. Reactions with sodium methoxide were inconclusive.

In the course of the work the following *alcoholates* of manganese and rhenium halides with alcohols were obtained: $MnCl_2,C_2H_5OH$; $MnCl_2,C_3H_7OH$; $MnBr_2,C_2H_5OH$; $MnBr_2,C_3H_7OH$; $ReCl_3,C_2H_5OH$; $ReCl_3,C_3H_7OH$. All these decomposed when strongly heated, usually giving off the alcohol accompanied by some alkyl halide and hydrogen halide, and the residue contained halogen.

No compounds were obtained with ether, but since compounds of tervalent rhenium were prepared, it was thought of interest to try to make the compound, $MnBr_3,3(C_2H_5)_2O$, described by Ducelliez and Raynaud (*Compt. rend.*, 1914, **158**, 576), with a view to converting it into a manganese trialkoxide. It was found, however, that when bromine is added to manganese under ether, reaction occurs and a lower layer of liquid separates, as Ducelliez and Raynaud state, but no compound of manganese tribromide was extracted. Manganese bromide was identified, together with certain organic bromine-containing compounds (*e.g.*, monobromoacetaldehyde).

EXPERIMENTAL.

Commercial absolute ethyl and *iso*propyl alcohols were dried over and then distilled from calcium shavings. When powdered manganese or rhenium was placed in either ethyl or *iso*propyl alcohol and heated under reflux for some hours, there was no reaction, and the filtrates left no residue on evaporation.

The alcohol compounds of the manganese halides were obtained by adding excess of manganese carbonate to a dry alcoholic solution of the hydrogen halide. The filtered solutions were placed in vacuum desiccators over calcium chloride, yielding crops of pink crystals of the salts with alcohol of crystallisation. These crystals, when separated, dried, and left in the vacuum desiccator for some days, underwent no further change.

The *compound*, $MnCl_2,C_2H_5OH$, obtained as bright pink crystals (Found: C, 13·75; H, 3·8; Cl, 41·1. $C_2H_6OCl_2Mn$ requires C, 14·0; H, 3·6; Cl, 41·3%), was stable in air and soluble in water and alcohol but not in ether. On heating, decomposition began below 100°, and at somewhat higher temperatures ethyl chloride was evolved, together with hydrogen chloride. The *compound*, $MnCl_2,C_3H_7OH$ (Found: C, 19·0; H, 5·5; Cl, 38·0. $C_3H_8OCl_2Mn$ requires C, 19·3; H, 5·3; Cl, 38·2%), was similar in appearance and properties. It began to lose alcohol at 113° in absence of air, and it fused below red heat, giving off some *iso*propyl chloride although the residue still contained much chloride.

The *alcoholate*, $MnBr_2,C_2H_5OH$ (Found: Br, 60·5. $C_2H_6OBr_2Mn$ requires Br, 61·3%), was obtained as pink crystals, which, when dry, showed no loss in weight when left in the desiccator for 14 days. By warming in a current of nitrogen, the alcohol was slowly lost, and anhydrous manganese bromide remained. When the compound was heated rapidly and more strongly, ethyl bromide and hydrogen bromide accompanied the alcohol driven off. The pink *compound*, $MnBr_2,C_3H_7OH$ (Found: C, 12·8; H, 2·9; Br, 57·7. $C_3H_8OBr_2Mn$ requires C, 13·1; H, 2·7; Br, 58·2%), behaved like the corresponding chloride.

The *compound* $ReCl_3,C_2H_5OH$ was obtained from an alcoholic solution of rhenium trichloride as brown-green crystals (Found : C, 6·65; H, 2·4; Re, 54·3 *; Cl, 31·0. $C_2H_6OCl_3Re$ requires C, 7·1; H, 1·8; Re, 55·0; Cl, 31·4%). It decomposed on heating without fusing, ultimately leaving no residue. It was soluble in water, alcohol, and ether. The aqueous solution at first gave no precipitate with silver nitrate, but addition of dilute nitric acid caused silver chloride to separate. With alkalis, and with water on boiling, rhenium sesquioxide separated, but was rapidly oxidised in air to the dioxide. The dried sesquioxide was more stable, and some of this oxide was soluble in hydrochloric acid even after several days' keeping.

$ReCl_3,C_3H_7OH$, similarly prepared from *iso*propyl alcohol (Found: Re, 51·8; Cl, 30·3. $C_3H_8OCl_3Re$ requires Re, 52·8; Cl, 30·2%), resembled the foregoing compound very closely in appearance and reactions.

Manganese Ethoxide.—A solution containing 3·44 g. of $MnCl_2,EtOH$ (above) in 30 c.c. of dry absolute alcohol was run into a sodium ethoxide solution obtained by dissolving 0·92 g. of clean sodium in 20 c.c. of dry ethyl alcohol in a flask protected from the atmosphere. The mixture was shaken, and kept for 24 hours, so that the precipitate of sodium chloride separated. The supernatant liquid was drawn off and allowed to evaporate slowly in a vacuum desiccator until dark brown crystals separated. These were collected and replaced in the desiccator for several days (Found : C, 32·8; H, 7·2; Mn, 37·6. Calc. for $C_4H_{10}O_2Mn$: C, 33·1; H, 6·9; Mn, 37·9%). The ethoxide reacted very readily with water, forming alcohol and white manganese hydroxide, which darkened on exposure to air. The compound was insoluble in ether but dissolved slightly in dry alcohol; the addition of even a trace of water, however, caused the separation of manganese hydroxide. When heated in air, the compound ignited, leaving a black residue. When it was heated out of contact with air, some ether appeared to be evolved, leaving a dark brown residue.

Manganese iso*Propoxide.*—This substance was similarly prepared by adding 3·72 g. of $MnCl_2,C_3H_7OH$ in 30 c.c. of *iso*propyl alcohol to a sodium *iso*propoxide solution (0·92 g. Na; 20 c.c. $Pr^{\beta}OH$). The filtrate, on slowly evaporating, left crystals of *manganese* iso*propoxide* (Found: C, 41·9; H, 8·4; Mn, 31·0. $C_6H_{14}O_2Mn$ requires C, 41·6; H, 8·1; Mn, 31·8%), which resembled the ethoxide in its behaviour towards water and acids, reacting vigorously with them. The alcoholic solution gave no precipitate either with manganese halides or with sodium ethoxide or *iso*propoxide.

Rhenium Triethoxide.—This was obtained as a dark brown solid by the interaction of 1·46 g. of rhenium trichloride in ether with a dry alcoholic solution of sodium ethoxide (0·34 g. Na; 30 c.c. EtOH). The filtrate, on evaporation, left the *ethoxide* (Found : C, 21·8; H, 4·4; Re, 58·7. $C_6H_{15}O_3Re$ requires C, 22·46; H, 4·68; Re, 58·1%). The compound was readily decomposed by water and by dilute acids and alkalis, alcohol and rhenium sesquioxide being first formed in each case. The substance was stable in dry air. On being heated in air it ignited, the black residue first formed gradually burning away. When heated out of contact with air, it began to decompose below 100°, impure rhenium remaining.

*Rhenium Tri*iso*propoxide.*—This light brown solid (Found : Re, 50·8. $C_9H_{21}O_3Re$ requires Re, 51·3%) was obtained similarly to the ethoxide (1·46 g. $ReCl_3$ in ether; 0·34 g. Na in 30 c.c. $Pr^{\beta}OH$), which it resembled in its properties. Hydrolysis with water produced *iso*propyl alcohol and rhenium sesquioxide. Dilute nitric acid also caused the separation of this oxide, but on being warmed with more acid, the precipitate dissolved to give a solution of per-rhenic acid.

The author is indebted to the Chemical Society for a research grant which has partly defrayed the cost of this investigation.

[*Received, June 24th,* 1937.]

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* Average of estimations as $ReO_2,2H_2O$ and as nitron per-rhenate.