# 525. *Studies of the Rare-earth Tungstates.*

By R. C. Vickery.

When precipitated from solution, tungstates of the lighter group of lanthanons * (La, Ce, Pr, Nd, Sm) appear amorphous and show previously undescribed colour changes on ignition. These are attributed to partial reduction to tungstites of varying composition which are finally reoxidised to stable crystalline tungstates. These phenomena are studied, and it is concluded that the precipitated tungstates have the generic formula $Ln_2O_3,3(H_2WO_4)$, being converted into the generally accepted $Ln_2(WO_4)_3$ structure only on heating.

Early investigations of lanthanon tungstates are recorded by French-Smith (" Uber Didym und Lanthan," Diss., Göttingen, 1876), Frerichs and Smith (*Annalen*, 1878, **191**, 331), Cossa and Zecchini (*Gazzetta*, 1879, **9**, 118; 1880, **10**, 1800), and Hitchcock (*J. Amer. Chem. Soc.*, 1895, **17**, 520). Later studies on these tungstates appear to have been conducted upon fused melts of tungstic and lanthanon oxides, little or no work having been carried out on the precipitation of the tungstates from solution. A re-examination of lanthanum tungstate has indicated previously undescribed reduction phenomena which occur on heating the compound; because of this, and the general advance of rare-earth chemistry since the first studies referred to above,

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* The designation " lanthanons " proposed by Marsh (*Quart. Reviews*, 1947, **1**, 126) is used here synonymously with " rare earths."

the examination was extended to cover the tungstates of all the lighter group of lanthanons (La, Ce, Pr, Nd, Sm).

Rare-earth tungstates have the generic formula $Ln_2(WO_4)_3$, established by the earlier workers from analyses of the ignited tungstates and confirmed by the later workers on thermal reactions. It will be shown, however, that this does not hold for the tungstates as precipitated.

Didier (*Compt. rend.*, 1886, **102**, 823) claimed to have proved the existence of chlorotungstates when the lanthanons were precipitated from chloride solutions by sodium tungstate, but many analyses of these compounds have failed to confirm his findings, and there would appear no doubt that the presence of chloride was due to insufficient washing.

The tungstates vary in colour according to the lanthanon present: white, pale buff, green, pink, and white for the La, Ce, Pr, Nd, and Sm compounds, respectively. Hitchcock (*loc. cit.*) stated that on the addition of sodium tungstate solution to one of lanthanum chloride in the presence of alcohol the rare-earth tungstate was obtained as a precipitate of delicate blue colour. The depth of the colour was stated to increase on ignition, but the author considers that the degree of blueness of the unignited precipitate is only that which is observed in starch sol or aluminium hydroxide gel; it is also considered that Hitchcock's lanthanum salt was impure, as the presence in the compound of a few tenths per cent. of praseodymium and neodymium imparts a definite blue tint to the precipitate.

## EXPERIMENTAL.

The lanthanon salts employed were all of at least 99·9% purity as shown by spectrographic analysis, and their oxides were believed to contain no metallic elements other than the lanthanons. The sodium tungstate was of "AnalaR" purity. The reagents were used as 10% aqueous solutions, the concentrations being based upon the anhydrous salts.

The lanthanon tungstates were prepared from sodium tungstate and lanthanon chloride solutions. The chloride solution was preferred to the sulphate or nitrate, because concurrent formation of sodium sulphate could lead to the partial precipitation of the lanthanon as the double sulphate, and with a nitrate solution the possible presence of a slight excess of free nitric acid would decompose the sodium tungstate, precipitating tungstic acid. In chloride solutions, any precipitation of tungstic acid by chlorides or small quantities of free hydrochloric acid in the absence of an oxidising agent is very slow.

Preliminary experiments were made to determine the effect on the product of variation in the mode of precipitation. The variations covered precipitation in the hot, in the cold, excess of either reagent, addition of the tungstate solution to the lanthanon, or *vice versa*. The precipitates obtained by these variations were washed many times by decantation, collected on sintered-glass crucibles under suction, and washed with small quantities of hot distilled water until the wash water was free from chloride and soluble tungstate. The precipitates were then dried over sulphuric acid, analysed, dried again at 105°, and again analysed. The results of this initial variation of precipitation conditions are shown in Table I, from which it is seen that under all conditions the ratio $Ln_2O_3 : WO_3$ remained the same within analytical error. The water content of the precipitate appeared to vary from the equivalent of $16H_2O$ when precipitated in the cold to $3H_2O$ in the hot; water equivalent to varying degrees of hydration was retained after drying over sulphuric acid but was lost at 105°, at which temperature all samples maintained a constant water content equivalent to $3H_2O$.

TABLE I.

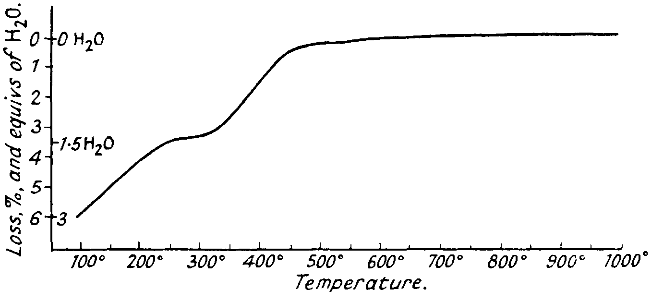
| | Analysis of ppt. after drying over $H_2SO_4$. | | | | | |
|---|---|---|---|---|---|---|
| | $Ln_2O_3$: | | $WO_3$: | | $H_2O$: | |
| Mode of precipitation. | %. | mols. | %. | mols. | %. | mols. |
| (1) Rapid addn. of equiv. quantity $Na_2WO_4$ to $LnCl_3$ at room temp. without agitation | 29·1 | 1·0 | 45·3 | 1·56 | 25·5 | 0·88 |
| (2) As (1) but with agitation | 31·0 | 1·0 | 48·5 | 1·57 | 20·3 | 0·66 |
| (3) As (1) but at 80° | 35·5 | 1·0 | 55·5 | 1·56 | 8·8 | 0·25 |
| (4) As (2) but at 80° | 36·0 | 1·0 | 56·0 | 1·56 | 8·0 | 0·22 |
| (5) As (2) but $LnCl_3$ added to $Na_2WO_4$ | 28·9 | 1·0 | 45·6 | 1·58 | 25·3 | 0·88 |
| (6) As (5) but at 80° | 36·5 | 1·0 | 56·3 | 1·54 | 7·0 | 0·19 |
| (7) As (4) but $Na_2WO_4$ added dropwise | 36·5 | 1·0 | 56·5 | 1·55 | 6·6 | 0·18 |
| (8) As (4) with 5% excess of $Na_2WO_4$ | 36·1 | 1·0 | 56·5 | 1·57 | 7·1 | 0·20 |
| (9) As (4) with 5% excess of $LnCl_3$ | 36·0 | 1·0 | 56·5 | 1·57 | 7·5 | 0·21 |
| (10) As (8) with $Na_2WO_4$ added dropwise; system digested 1 hr. at 80° | 36·6 | 1·0 | 57·4 | 1·57 | 6·0 | 0·16 |
| (11) As (10) with 2 hrs.' digestion | 36·7 | 1·0 | 57·3 | 1·56 | 6·0 | 0·16 |
| After drying at 105° all samples contained: | 36·7±0·25. | | 57·3±0·4. | | 6·0±0·2. | |
| Calc. for: | | | | | | |
| $Ln_2(WO_4)_3$ | 39·05 | | 60·95 | | — | |
| $Ln_2O_3,3WO_3,3H_2O$ | 36·7 | | 57·3 | | 6·0 | |
| $Ln_2O_3,3WO_3,16H_2O$ | 29·08 | | 45·4 | | 25·52 | |

(Average atomic weight for "Ln": 140.)

In order to study the possible formation of hydrates, precipitation of lanthanum and neodymium tungstates was carried out at temperature intervals of 5° from 20° to 100°, the dehydration and vapour-pressure curves studied, and the product analysed. The dehydration values were obtained by direct weighing after the samples had been kept at various temperatures for 8 hours, and the vapour-pressure data were obtained by the dew-point method.

FIG. 1.

*Average dehydration curve for lanthanon tungstates.*

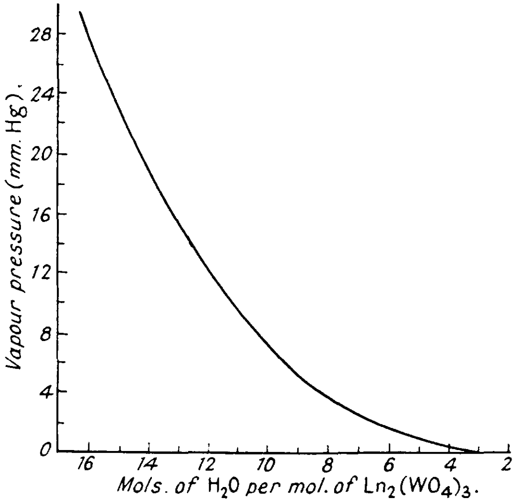


In the preparation of lanthanum and neodymium tungstates, precipitation was carried out by the dropwise addition of a 5% excess of the tungstate solution to that of the lanthanon under vigorous agitation at 80°, and the precipitates were digested at 80° for 2 hours before decantation, washing, filtration, etc., as above. Hitchcock used alcohol to ensure quantitative precipitation but this was not found to be necessary. The precipitates were dried over sulphuric acid for the dehydration studies. This mode of preparation of the lanthanon tungstates was employed for further work except that they were dried at 105°.

Precipitation of the tungstates is usually immediate, but on occasion a slight delay was noted in the commencement of precipitation which might indicate a non-ionic reaction.

FIG. 2.

*Vapour-pressure curve for lanthanon tungstates at* 35°.



From analysis and dehydration (Fig. 1) and vapour-pressure data (Fig. 2) it is seen that no evidence was found for any except trihydrates. From the slope of the (35°) vapour-pressure curve it is evident that one may regard water present above the trihydrate level as being consistent with zeolitic water or the interstitial hydrates reported by Wylie (*J.*, 1947, 1687). This consideration is also in keeping with the hygroscopicity of the semi-ignited tungstates (see below). The water content of the tungstates decreased smoothly with increasing temperature until the trihydrate was reached, but on further dehydration an abrupt deflection was obtained at *ca.* 275°, equivalent to a sesquihydrate. Vapour-pressure studies could not be carried to this level, but repetition of the dehydration experiments exactly reproduced previous results.

The solubilities of the tungstates in water vary slightly throughout the series (see Table II), increasing with atomic number but nevertheless remaining low. All the tungstates are soluble in phosphoric, citric, and tartaric acids, but insoluble in acetic acid. Mineral acids decompose them with formation of the corresponding lanthanon salt and deposition of tungstic acid. Alkali hydroxides or carbonates decompose the tungstates with formation of the corresponding lanthanon hydroxide or carbonate and alkali tungstate : the reaction velocities in this sequence appear to be in the order of $Na^+ > K^+ > NH_4^+$ and $OH^- > CO_3^{--}$.

On ignition of the tungstates a series of colour changes is observed at fairly definite temperatures, the exact colours produced at any temperature depending upon the particular lanthanon (see below). The ignited tungstates have a reactivity in the same order as, but less than, that of the unignited compounds; aqueous solubilities are rather lower for the ignited than for the unignited tungstates (Table II). Complete decomposition of the ignited tungstates by alkali hydroxides or hydrochloric, nitric, or sulphuric acid is difficult, but a mixture of phosphoric and sulphuric acids ("Spekker" acid) effects dissolution much more rapidly and retains the tungstic acid in solution, in agreement with the work of Rogers and Smith (*J. Amer. Chem. Soc.*, 1904, **26**, 1482), who found that the inclusion of a pentoxide in the molecule rendered soluble some complex tungstates. The densities of the ignited and unignited tungstates vary sequentially (Table III).

TABLE II.

*Solubilities in water (g./100 ml.).*

| | Unignited tungstates. | | Ignited tungstates. | |
|---|---|---|---|---|
| | 20°. | 100°. | 20°. | 100°. |
| La ...... | 0·014 | 0·0194 | 0·001 | 0·001 |
| Ce ......... | 0·014 | 0·020 | 0·001 | 0·001 |
| Pr ......... | 0·020 | 0·025 | 0·002 | 0·002 |
| Nd ...... | 0·021 | 0·027 | 0·003 | 0·003 |
| Sm ...... | 0·025 | 0·032 | 0·003 | 0·004 |

TABLE III.

*Variation of colour and density with temperature.*

| | La. | | Ce. | | Pr. | | Nd. | | Sm. | |
|---|---|---|---|---|---|---|---|---|---|---|
| Temp. | Colour. | *d.* | Colour. | *d.* | Colour. | *d.* | Colour. | *d.* | Colour. | *d.* |
| 100° | white | 3·18 | buff | 3·00 | green | 2·80 | pink | 2·70 | white | 2·45 |
| 200° | white | — | buff | — | green | — | pink | — | white | — |
| 300 | tan | 5·2 | tan | — | green | — | lilac | 3·3 | yellow | — |
| 400 | yellow | — | tan | — | khaki | — | grey | — | buff | — |
| 500 | brown | 7·6 | brown | 7·4 | brown | 6·4 | indigo | 5·0 | brown | 4·4 |
| 600 | olive | 7·8 | tan | — | black | 6·9 | indigo | 5·3 | black | 4·7 |
| 700 | green | — | yellow | 6·3 | brown | — | grey | — | brown | — |
| 800 | yellow | — | yellow | — | yellow | — | grey | — | tan | — |
| 900 | white | — | stone | — | green | — | lilac | — | white | — |
| 1000 | white | 6·16 | stone | 5·8 | green | 5·14 | lilac | 4·5 | white | 4·1 |

*Thermal Phenomena.*—The colour changes mentioned above are given in Table III. At first, the samples (5—10 g.) were heated in open silica crucibles over a Bunsen flame, the crucibles and contents being occasionally shaken. For finer observation of temperature and colour changes, however, heating experiments were finally carried out with the tungstate charges in silica boats in an electric tube-furnace. The temperature of the furnace was determined by a thermocouple inserted through one hole of a stopper, a second hole carrying a delivery tube for attachment to a nitrogen cylinder. Temperatures, although not accurately standardised, are considered to be accurate to $\pm 10°$ in the high ranges.

In the straight ignition runs samples of the charges were taken at 100° intervals by means of a small silica scoop fused to a long silica rod; these samples were placed in small open silica capsules and allowed to cool in a calcium chloride desiccator before examination for colour and in some cases density. Samples of charges ignited in nitrogen were withdrawn in the silica scoop from one end of the furnace tube whilst a flow of nitrogen was maintained from the other, and were similarly cooled and dried

In all series of air-ignited tungstates degradation from the darkest colour to a lighter at high temperature was exothermic as shown by a sudden glowing of the charge, also, up to the temperature of darkest coloration, the tungstates exhibited varying degrees of hygroscopicity, which was in all cases lost when the final pale colour was attained. The variation in density (determined pyknometrically against water) of the unignited and fully ignited compounds was found to be related to the colour, the darkest compounds having the highest density (Table III); also, the fully ignited tungstate was crystalline whereas the unignited salt was apparently amorphous.

By heating the tungstates in an atmosphere of oxygen-free nitrogen (see above) it was possible to keep them at the intermediate phases indicated by their darkest colours and to determine the properties of these stages. Maximum ignition in nitrogen yielded only the darkest products, but on replacement of the nitrogen by air or oxygen, the progression to the final pale colour was resumed. That these intermediate stages were indicative of reduction was shown, and the degree of reduction determined, by solution of the samples in 50% "Spekker" acid in the presence of potassium dichromate solution in an inert atmosphere and titration of the excess of dichromate with a ferrous salt. Although reduction effects were proved, no definite stages could be established (Table IV).

Qualitative studies on the reactions of these reduced compounds showed that normal reactions, *i.e.*, comparable to those of the unignited and fully ignited tungstates, were of rates apparently dependent upon reoxidation and temperature of ignition; in an atmosphere of nitrogen, decomposition by sulphuric acid was very slow; also, rates of solution in "Spekker" acid apparently varied not only with the degree of reduction but also with atomic number of the lanthanon, decreasing as this increased.

TABLE IV.

*Actual and theoretical reduction.*

| Tungstate. | Temp. | O, %, taken up. | Reduction, %. | Tungstate. | Temp. | O, %, taken up. | Reduction, %. |
|---|---|---|---|---|---|---|---|
| La ........... | 300° | 8·25 | 20·15 | Pr ........... | 600° | 2·0 | 4·70 |
| | 500 | 1·92 | 4·52 | | 1000 | nil | nil |
| | 600 | 2·71 | 6·35 | | | | |
| | 950 | nil | nil | Nd ......... | 400 | 6·3 | 14·7 |
| | | | | | 550 | 1·5 | 3·53 |
| Ce ........... | 300 | 7·83 | 18·4 | | 650 | 1·15 | 2·71 |
| | 500 | 1·53 | 3·6 | | 950 | nil | nil |
| | 900 | nil | nil | | | | |
| | | | | Sm ......... | 500 | 1·5 | 5·53 |
| | | | | | 900 | nil | nil |

| Theoretical : | | O, %, taken up. | Reduction, %. |
|---|---|---|---|
| $Ln_2O_3,3WO_3$ | $\longrightarrow Ln_2O_3,3W$ ..................... | 42·3 | 100 |
| | $Ln_2O_3,3WO$ ................... | 9·42 | 22·3 |
| | $Ln_2O_3,3WO_2$ .................. | 4·7 | 11·2 |
| | $Ln_2O_3(WO_2,W_2O_5)$ ......... | 3·13 | 7·4 |
| $2(Ln_2O_3,3WO_3)$ | $\longrightarrow 2Ln_2O_3,3WO_2$ ............... | 2·35 | 5·56 |

*Discussion and Conclusions*.—Consideration of the sequence of colour changes and other relevant data suggests that partial reduction of the tungstate occurred on heating, leading to the changes of colour observed before the final reoxidation to the compounds $Ln_2(WO_4)_3$.

The retention of the equivalent of $3H_2O$ in the molecule would appear to be initial evidence of an $H_2WO_4$ component in the total tungstate molecule as precipitated, *i.e.*, $Ln_2O_3,3H_2WO_4$, the bonds between the two components being very loose and indicative of a lattice with many holes in it. Such a formation would be borne out by the behaviour of the tungstate on heating. Tungstic acid is known (Mellor, " Comprehensive Treatise, etc.," Vol. XI) to lose its water at *ca.* 300°, and in the presence of metallic oxides this temperature may be slightly lowered ; further, the tungstate molecule exhibits reduced oxides before final conversion into $WO_3$ ; in the presence of some metallic oxides this final oxidation does not occur, but that it does occur in this case is indicated by the final colour change and by analysis. One could postulate also the formation of a molecule containing lanthanon hydroxide instead of tungstic acid, *i.e.*, $Ln(OH)_3,(WO_3)_3$, which also would account for the retention of the equivalent of $3H_2O$, but in this case a higher temperature would be required for the conversion of the hydroxide into oxide before formation of the tungstate in the known way; further, this would not account for the colour changes observed or for the dehydration deflection at 275°, which is itself accounted for by the presence of metallic oxides ($Ln_2O_3$) with the tungstic acid. The loose nature of the bonds would also be confirmed by the fact that tungstates known to be strongly bound do not undergo change of colour, etc., on ignition.

The colour changes produced on heating are directly comparable with those observed by Glemser and Sauer (*Z. anorg. Chem.*, **1943**, **252**, 144) during the ignition of tungstic acid. These workers found blue, olive, brown, etc., phases at various temperatures, and the colours produced on heating lanthanon tungstates are closely correlated with mixtures of these colours with those of parent lanthanons.

The densities found for the ignited lanthanum and cerium tungstates agree reasonably well with data given by other workers, but data for the other lanthanons are lacking. The solubilities obtained differ slightly from those reported by Hitchcock for lanthanum, etc., but she did not state the temperature at which she ignited her specimens, and from the data given above it is evident that this is of great importance.

It is considered, therefore, that the compound precipitated on addition of tungstate solution to one of a lanthanon chloride conforms to the generic formula $Ln_2O_3,3(H_2WO_4)$ and that this is converted on heating into $Ln_2(WO_4)_3$ *via* intermediate tungstites. *X*-Ray data on the structural characteristics of the original, reduced, and finally oxidised tungstates should afford interesting information.

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