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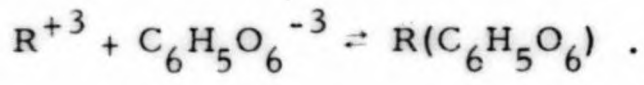
TRICARBALLYLIC ACID (PROPANE-1, 2, 3-TRICARBOXYLIC ACID) -
A NEW GRAVIMETRIC REAGENT FOR RARE EARTHS*

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Tricarballylic acid (propane-1, 2, 3-tricarboxylic acid) has a structure similar to that of citric acid, except that it lacks the hydroxyl group attached to the middle carbon atom. Properties of the rare-earth citrates have been used very successfully in the separation of rare earths by ion exchange methods; consequently, it was deemed advisable to study the rare-earth compounds which form with the anion of tricarballylic acid.

It was assumed a priori that a tricarballylate anion would behave as a tridentate ligand, and that the following reaction would take place when the rare-earth cations and the tricarballylate anion were combined in a 1:1 ratio



The resulting compounds were found to be extremely insoluble, thus it appeared that the reaction proceeded almost completely in the right-hand direction. The products were found to correspond to the above formula, except for a definite degree of hydration. To confirm the

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amount of hydration, thermal decomposition of the compounds by the thermogravimetric method was investigated; and, to determine the intrinsic solubilities of different rare earth tricarballylates, solubilities at two different temperatures were studied(1). The solubility studies, conducted at 20 and 60°C, showed that the heavy-rare-earth compounds (samarium through lutecium) are extremely insoluble (solubility below .005 gm/100 gm of water), and that the precipitation during formation is quantitative. The light rare earths (La, Ce, Pr and Nd) were found to form more soluble compounds. The precipitation during formation was not quantitative.

The heavy-rare-earth tricarballylates were best precipitated, in the pH range 5.5-7.0, by diammonium acid tricarballylate. The precipitates were flocculent and voluminous at first; but on standing became granular and crystalline in nature. The heavy-rare-earth tricarballylates were found to be less soluble than the corresponding rare-earth oxalates. When assayed as oxide, after precipitation and ignition at 900°C, rare-earth tricarballylates gave uniformly reproducible quantitative yields of oxide, higher than those obtained by the oxalate method.

It was found that calcium, barium and zinc did not form insoluble compounds with diammonium tricarballylate, and successful quantitative separations of these elements from rare earths were obtained. In the cases with calcium and zinc, double precipitation of the rare-earth tricarballylate was necessary in order to obtain precipitates of high spectroscopic purity; but virtually all of the Ba was separated by

a single precipitation.

Quantitative separation from sodium, which is almost impossible when rare earths are precipitated as oxalates, was also studied.

Experimental

Reagents

1. Rare-earth stock solutions - Rare-earth stock solutions of approximately 0.1M concentration were prepared by dissolving a 99.99% pure rare-earth oxide in hydrochloric acid, evaporating the solution to incipient dryness, and diluting the residue to 1000 ml with distilled water.
2. Diammonium acid tricarballoylate - The tricarballoylic acid (supplied by K & K Laboratories, Inc.) was recrystallized, and a 4% solution was made by dissolving the required amount of acid in distilled water. The acid was two-thirds neutralized by adding ammonium hydroxide.
3. Calcium solutions - Various stock solutions of calcium were prepared by dissolving reagent grade CaO in hydrochloric acid and diluting with distilled water. The strength of each solution was determined by the calcium oxalate-permanganate method.
4. Barium solution - An approximately 0.1N solution was prepared by dissolving reagent grade $\text{Ba}(\text{NO}_3)_2$ in distilled water. The solution was standardized by the sulphate method.
5. Zinc solution - An approximately 0.1N solution was prepared by dissolving $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in distilled water. The solution was

standardized both by titration with EDTA and by the pyrophosphate method.

Comparative Estimation of Rare Earths by the Oxalate
and Tricarballylate Methods

Tricarballylate Method

Ten milliliter of rare-earth stock solution was pipetted into a 250 ml beaker and diluted to 100 ml by the addition of distilled water. The solution was warmed, and 4% diammonium tricarballylate solution was added, drop by drop with constant stirring, until the precipitation was complete. The mixture was either left overnight or heated on a water-bath for one hour. The precipitate was flocculent and voluminous at first, but became granular and crystalline on standing. It was filtered on a quantitative filter paper, washed with cold distilled water until free from Cl^- , dried and ignited in a previously weighed crucible at 900°C until a constant weight was obtained. Each experiment was done in duplicate. See Table 1.

Oxalate Method

The usual oxalate precipitation and assaying method was followed. The results are given in Table 1. From the results in Table 1, it was found that heavy-rare-earth tricarballylates, from samarium, were less soluble than the corresponding oxalates.

Separation of Bivalent Elements from Rare Earths
by the Tricarballylate Method

It was observed that bivalent elements like calcium, barium, strontium, magnesium, zinc and lead do not form insoluble compounds with diammonium acid tricarballylate in the neutral or slightly acid media in which rare earths are precipitated.

Taking advantage of this observation studies were made concerning the successful separation of calcium, barium and zinc from rare earths.

Separation of Ca from Rare Earths

The rare earths were mixed with calcium in approximately 10:1 proportion and the following procedure was employed.

Procedure - 10 ml of stock rare-earth solution and 10 ml of stock calcium solution were pipetted into a 250-ml beaker and diluted to 150 ml with distilled water. The solution was heated to 50-60°C, and diammonium tricarballylate solution (4%) was added, drop by drop with constant stirring, until no further precipitation occurred. The mixture was allowed to stand overnight. Then the precipitate was filtered on a quantitative filter paper and washed free from calcium with cold distilled water (tested with oxalic acid). The residue was transferred completely into the filter paper, dried and ignited in a previously weighed crucible to the oxide in a muffle furnace at 900°C, until a constant weight was obtained. The filtrate and washings from the rare-earth precipitations were collected in a 400-ml beaker. One or two drops of methyl red indicator were added, and the solution was heated

to boiling. It was removed from the heat, and 15 ml of 4% ammonium oxalate solution was added with constant-stirring; then 1% NH_4OH solution was added, very slowly with constant stirring, until the solution became alkaline to methyl red. It was allowed to stand overnight. The calcium oxalate thus obtained was estimated by the standard permanganate method.

The results obtained by the above procedure, though they may be analytically suitable as would be evident from Table 2, were not suitable for separation in the strictest sense, as both the rare earths and calcium were found to be contaminated by co-precipitation of the other constituent.

To remove the contamination of calcium from the rare earths, a double precipitation of the rare earths as tricarballylate was done. The rare-earth tricarballylate residues obtained after the first precipitation were dissolved in hot dilute hydrochloric acid and were reprecipitated by neutralizing with dilute ammonium hydroxide and then adding 5 ml of the diammonium tricarballylate. The residue was filtered, dried and was ignited to the oxide as before. The filtrate and washings were combined with the filtrate from the first precipitation and calcium was estimated by the oxalate permanganate method. The results are given in Table 3.

Separation of Ba from Rare Earths

Barium was separated from rare earths by a single precipitation of rare earths with diammonium tricarballylate. Very little or no contamination by co-precipitation was observed. The procedure of separation was the same as that for separation from calcium. Barium was estimated from the filtrate of the rare-earth tricarballylates by the sulphate method. The results are given in Table 4.

Separation of Zinc from Rare Earths

When rare earths were separated from zinc by a single precipitation with diammonium tricarballylate and the zinc was estimated by the pyrophosphate method, it was observed that the amount of rare-earth oxide was always higher than the amount added but that the amount of zinc was more or less same as the amount taken. Moreover, on spectroscopic analysis, the rare-earth oxides were found to be heavily contaminated with zinc. It was suspected that the method of estimation of zinc (pyrophosphate method) was compensating for zinc lost by coprecipitation with the rare-earth tricarballylate.

It was decided to double precipitate the rare earths as the tricarballylate, as in the case of calcium, and to estimate the zinc in the combined filtrates by complexometric titration with EDTA. The results are given in Table 5.

Separation of Sodium from Rare Earths

When rare earths were precipitated as oxalates in the presence of alkali metal ions and were ignited and weighed as oxide, the results were always high, the porcelain crucibles were attacked and spectroscopic analysis showed a high degree of contamination by alkali metals.

When the rare earths were precipitated as tricarballates in the presence of alkali metal ions, however, reproducible results were obtained with no appreciable contamination by alkali metals (confirmed by spectroscopic analysis, and there was no corrosion of the crucibles. Rare earths were precipitated both by the oxalate and tricarballate methods under identical conditions in the presence of the same amount of NaCl. The results are given in Table 6.

Whether a definite compound is formed, or not, during the precipitation of rare earths as oxalates in the presence of alkali metal ions is not known, but it is known that, when they are precipitated with oxalate ion, rare earths form two species of oxalates, $R(C_2O_4)^+$ and $R(C_2O_4)_2^-$, which then combine to form $R_2(C_2O_4)_3$. We assume that in the presence of alkali metal ions a double compound of the type $MR(C_2O_4)_2$ is formed which, when ignited, decomposes to R_2O_3 and Na_2CO_3 . The latter is responsible for the high results and the corrosion of the crucibles. The matter is still under investigation.

Out thanks are due to Dr. V. A. Fassel and his group for all the spectroscopic analyses.

References

- (1) Asim K. Gupta and Jack E. Powell, "Some Observations on Rare-Earth Salts of Tricarballic Acid (propane 1, 2, 3-tricarboxylic acid)-Hydration and Solubilities of the Compounds", USAEC Rept. IS-657 (1963).

Table 1*

Comparison of the recovery of rare-earth oxides by the oxalate and tricarballylate methods.

Oxide	Oxalate method	Tricarballylate method
Sm_2O_3	.1747 ± .0002	.1757 ± .0001
Eu_2O_3	.1753 ± .0001	.1763 ± .0001
Gd_2O_3	.1745 ± .0002	.1760 ± .0001
Tb_4O_7	.1823 ± .0002	.1823 ± .0001
Dy_2O_3	.1889 ± .0001	.1893 ± .0002
Ho_2O_3	.1864 ± .0001	.1868 ± .0001
Er_2O_3	.0882 ± .0002	.0896 ± .0001
Tm_2O_3	.1917 ± .0001	.1926 ± .0001
Yb_2O_3	.2019 ± .0001	.2026 ± .0001
Lu_2O_3	.1888 ± .0002	.1901 ± .0001

* The figures in Table 1 are the average results of several estimations.

Table 2*

Results of the separation of rare earths and calcium
by the tricarballylate method.

element	Rare-earth oxide		calcium contamination in ppm	Calcium oxide	
	added-gm	found-gm		added-gm	found-gm
Sm	.1757	.1755	2000	.019	.0186
Sm	.0878	.0879	2000	.0621	.0613
Eu	.1763	.1762	2000 - 5000	.019	.0186
Eu	.0881	.089	"	.0621	.0613
Gd	.1760	.1757	6000	.019	.0185
Gd	.088	.0891	"	.0621	.0613
Tb	.1823	.1836	>> 6000	.019	.0185
Tb	.0912	.0926	"	.031	.0307
Dy	.1893	.1898	5000	.019	.0184
Dy	.0947	.0953	"	.031	.0308
Ho	.1868	.1874	5000	.019	.0184
Ho	.0934	.0935	"	.031	.0308
Er	.0896	.0995	> 5000	.019	.019
Er	.0448	.0444	"	.031	.0311
Tm	.1926	.1924	5000	.031	.0308
Tm	.0963	.0965	"	.031	.0308
Yb	.2026	.2036	5000	.031	.0308
Yb	.1013	.1018	"	.031	.0309
Lu	.1901	.1900	5000	.019	.019
Lu	.095	.0945	"	.031	.031

* The results given in this table are the average results of several estimates.

Table 3*

Results of the separation of rare earths and calcium employing a double precipitation of the rare earths as the tricarballylate.

element	Rare-earth oxide		calcium contamination in ppm	Calcium oxide	
	added-gm	found-gm		added-gm	found-gm
Sm	.1751	.1748	100	.0311	.0315
Eu	.1755	.1758	500	.0311	.0313
Gd	.1748	.1751	200	.0311	.0312
Tb	.1825	.1831	300	.0311	.031
Dy	.1894	.1898	300	.0311	.031
Ho	.1868	.1873	300	.0311	.0311
Er	.0893	.0887	100	.0311	.0313
Tm	.1926	.1924	100	.0311	.0312
Yb	.2020	.2022	300	.0311	.0311
Lu	.1898	.1894	150	.0311	.0312

* The results are the averages of several estimations.

Table 4*

Results of the separation of rare earths and barium
by the tricarballylate method.

element	Rare-earth oxide		barium contamination ppm	Barium	
	added-gm	found-gm		added-gm	found-gm
Sm	.1751	.1752	50-100	.069	.0689
Eu	.1755	.1758	"	.069	.0685
Gd	.1748	.1747	"	.069	.0689
Tb	.1825	.1823	"	.069	.0689
Dy	.1894	.1896	"	.069	.0689
Ho	.1867	.1867	"	.069	.0689
Er	.0893	.0894	"	.069	.0689
Tm	.1926	.1925	"	.069	.0692
Yb	.2020	.2023	"	.069	.0689
Lu	.1898	.1900	"	.069	.0689

* We had no barium standard. The lines obtained were very weak (trace-impurity-not more 50-100 ppm). The results given are the averages of several estimations.

Table 5*

Results of the double precipitation of rare-earth tricarballylates
in the presence of zinc.

element	Rare-earth oxide		zinc contamination	zinc	
	added-gm	found-gm		added-gm	found-gm
Sm	.1751	.1753	not detected	.065	.065
Eu	.1755	.1754	trace detected	.065	.0649
Gd	.1748	.1750	trace detected	.065	.065
Tb	.1825	.1828	trace, interference	.065	.0649

* The rare-earth oxides were examined spectroscopically for zinc. The above results are average of several estimations.

Table 6*

Results of the tricarballylate and oxalate precipitations
of selected rare earths in the presence of sodium ion.

element	Rare-earth oxide		sodium contamination	
	tricarballylate found-gm	oxalate method found-gm	tricarbally- late method	oxalate method
Sm	.1751	.1754 ± .0001	100 ppm	very strong
Dy	.1894	.1895 ± .0001	100 ppm	very strong
Lu	.1901	.1902 ± .0001	100 ppm	1.5 - 2%

* The results are the averages of several estimates.

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