[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Observations on the Rare Earths. XXXIII. Studies in Basicity[1]

BY G. R. SHERWOOD WITH B. S. HOPKINS

The relative basicities of the members of the rare earth group are of fundamental importance, because many of the methods of fractionation are based upon this characteristic of the individual members of the group. It is frequently true that the methods employed for removing the last and most persistent impurities are methods which depend on differences in basicity. Hence it is important to define as sharply as possible the order of decreasing basicity within the group.

Historical.—The order of decreasing basicity as reported by various authorities is given in Table I, which for convenience is divided into three zones. It is to be noted that there is little doubt concerning the order of basicity in both Zones 1 and 3, while in Zone 2 it is uncertain whether europium and gadolinium are more or less basic than samarium. Katz and James[2] have found that these elements differ in basicity much less than other adjacent members of the group. This fact and the natural difficulties in following the course of both gadolinium and europium during fractionation undoubtedly account for the confusion in results.

A physico-chemical study of the rare earth sulfates has recently been made by Brauner and Švagr.[2a] They have determined the relative basicities of certain sulfates by measuring their effect on the inversion of saccharose and the hydrolysis of methyl acetate. They find a gradual decrease in basicity in passing from lanthanum to cerium, praseodymium, neodymium and samarium. Gadolinium is observed to have a basicity close to that of lanthanum, from which it is reasoned that gadolinium is the first member of a third group of rare earths which should be placed in the ninth row in the Periodic Table.

An outstanding study in relative basicity has been published recently by Günther Endres,[3] who determined the solubility product from the amount of rare earth hydroxide which is precipitated when each individual member of the group is mixed with a solution of ammonia buffered with ammonium nitrate and cadmium nitrate. This method gives large differences in basicity which may be expressed numerically using the basicity of $Y(OH)_3$ as unity

Atomic number.......	57	59	60	62	64	39	66
Element..............	La	Pr	Nd	Sm	Gd	Y	Dy
Basicity ratio.........	1300	80	47	8	3.4	1	0.5

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(1) Summary of a thesis presented to the Graduate School of the University of Illinois by G. R. Sherwood in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Katz and James, THIS JOURNAL, **36**, 679 (1914).

(2a) B. Brauner and E. Švagr, *Coll. Czecho. Chem. Communications*, **4**, 49, 239 (1932).

(3) Endres, *Z. anorg. allgem. Chem.*, **205**, 321 (1932).

The work of Goldschmidt[4] and Grimm[5] and their co-workers makes possible an arrangement of the rare earths based upon their ionic radii. Endres points out that the differences in ionic radii are almost exactly similar to the differences in basicities which he obtains. Hence he concludes that

TABLE I

	A[a]	B[b]	C[c]	D[d]	E[e]	F[f]	G[g]
Zone 1						Dy	
	La	La		La	La	La	La
	Ce^{+++}	Ce^{+++}		Ce^{+++}			
	Pr	Pr		Pr	Pr	Pr	Pr
	Nd	Nd		Nd	Nd	Nd	Nd
	Y	Y					
Zone 2		Eu					
		Gd	Gd		Gd		
	Sm	Sm	Sm	Sm	Sm	Sm	Sm
	Eu			Eu			
	Gd			Gd			Gd
Zone 3	Tb	Tb	Tb	Tb	Y	Y	Y
	Dy	Dy		Dy	Dy		Dy
	Ho	Ho		Y			
	Er	Er		Er	Er		
	Tm	Tm		Tm			
	Yb	Yb		Yb			
	Lu	Lu					
	Sc	Sc					
	Ce^{++++}						

[a] Friend, "Textbook of Inorganic Chemistry," Vol. IV, p. 258. This order is based on thermal decomposition of nitrates, precipitation of hydroxides and hydrolysis of sulfates. Brauner and Švagr agree with this order for the first seven elements, but believe that a new series starts with gadolinium, which is nearly as basic as lanthanum.

[b] Order indicated by Hevesy, "Die seltenen Erden vom Standpunkte des Atombaues," pp. 29, 51, based on ammonia precipitation; Levy, "Rare Earths," p. 113, based on ammonia precipitation and decomposition of nitrates; Spencer, "Metals of the Rare Earths," p. 127, based on ammonia precipitation; and Britton, *J. Chem. Soc.*, **127**, 2142 (1925), based on precipitation with sodium hydroxide.

[c] Order of precipitation by ammonium hydroxide as found by de Boisbaudran [*Compt. rend.*, **111**, 393 (1890)], Benedicts [*Z. anorg. Chem.*, **22**, 393 (1900)] and by Brinton and James [THIS JOURNAL, **43**, 1446 (1921)]; the last named authors found the same order in studying the dissociation of the sulfates.

[d] Brinton and James, hydrolysis of the carbonates [THIS JOURNAL, **43**, 1451 (1921)] and Katz and James, hydrolysis of the sulfates [*ibid.*, **36**, 779 (1914)].

[e] Meyer and Bodländer, electrometric determination of hydrogen-ion concentration as a measure of hydrolysis of the chlorides [*Naturwissenschaften*, **2**, 786 (1914)].

[f] Kleinheksel and Kremers, acidity of rare earth chloride solutions [THIS JOURNAL, **50**, 959 (1928)].

[g] Günther Endres, precipitation with ammonia in the presence of ammonium nitrate and cadmium nitrate [*Z. anorg. allgem. Chem.*, **205**, 321 (1932)].

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(4) Goldschmidt, Barth and Lunde, *Det. norsk. Vid. Akad. i Oslo. Skr. I M-N Kl*, No. 7 (1925).

(5) Grimm and Wolff, *Z. physik. Chem.*, **119**, 226 (1926).

changes in basicity and ionic radius are parallel throughout the entire rare earth group and therefore the order of decreasing basicity is the order of increasing atomic number. Klemm[6] calls attention to the fact that this order is in harmony with that which he published in 1929[7] but he objects to the extension of the relationship between basicities and atomic radii on the ground that Endres' meager experimental data do not justify such a broad conclusion.

Studies of this sort are extremely valuable for the light they throw upon the atomic structures and fundamental relationships which exist between the members of the rare earth group. The actual work of separating these elements from each other must depend upon their behavior in the complex mixtures in which they are always found in nature. Consequently our present study of relative basicities has been confined to the problem of determining the order in which the members of the group are removed from a mixture by fractionation methods which depend upon basicity.

Experimental

Since separations by means of fractional precipitation or thermal decomposition are slow and poorly adapted to the fractionation of highly complex mixtures, the raw material selected for this study consisted in the relatively simple fractions obtained by a preliminary process of fractional crystallization. Residues from the gas mantle factory were dissolved in nitric acid and the cerium removed by potassium permanganate. The removal of cerium was considered necessary because cerous and ceric salts differ widely in basicity, hence the position of this element in a basicity series will depend upon conditions. The actual position of cerium is a matter of little practical importance because it can readily be removed almost quantitatively from other members of the rare earth group by the hydrolysis of the ceric salts. For this study a total of 20 kg. of cerium-free rare earth oxides were prepared and subjected to fractional crystallization as the double magnesium nitrate, followed in some cases by fractionation as the bromate or as the simple nitrate. In every case the fractionation was continued until certain fractions, when examined spectroscopically, were found to contain one principal constituent with a relatively small proportion of adjacent members. These were selected for treatment to determine the order of precipitation of their metals.

The method selected was the sodium nitrite precipitation method of Holden and James[8] because it gives a rapid separation of the members of the group. It is readily applied to all members of the group and it lends itself easily to carefully selected conditions; so it may be relied upon to give uniform results throughout the entire range. Since the purpose of this investigation was to determine the order of decreasing basicity and since the differences especially in Zone 2 were slight, it was decided to modify the procedure in such a way as to magnify those differences. As usually carried out a method of fractional precipitation depends upon the separation produced by a single precipitation. We have found that much sharper separations can be produced by the use of a plan similar to that used in fractional crystallization. The procedure followed may be described as follows: The selected mixture is divided into three nearly equal fractions by precipitation with sodium nitrite. These are dissolved in the smallest possible quantity of hydrochloric acid and evaporated just to dryness on the steam-

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(6) Klemm, *Z. anorg. allgem. Chem.*, **209**, 321 (1932).

(7) Klemm, *ibid.*, **184**, 345 (1929).

(8) Holden and James, THIS JOURNAL, **36**, 1418 (1914).

bath. Fraction 1 is dissolved in water and about half its contents again precipitated with sodium nitrite. This precipitate is filtered out and the mother liquor is added to Fraction 2, which is then about half precipitated with sodium nitrite. This process is represented diagrammatically in Fig. 1, the solid arrows showing the disposition of the precipitate and the dotted arrows indicating the path of the mother liquor. Since Fraction 1 rapidly decreases in size we have found it desirable to start with two or more identical quantities of material in separate series and then combine the parallel fractions when they become too small for convenience.

In carrying out this process it has been more satisfactory to boil the solution vigorously in an open vessel than to agitate with a jet of steam. The acidity of the solution to which the sodium nitrite is added is very important. If too much or too little acid is present the precipitate does not form or it will be colloidal and unfilterable. If the solution of rare earth salts is made slightly acid, a strong solution of sodium nitrite added and the mixture boiled, there appears a granular precipitate which settles quickly and filters readily unless the concentration of sodium salts is too high. Colloidal precipitates, which are probably sodium double salts, appear whenever a fraction contains a large excess of sodium compounds. For this reason the most basic members of the series were allowed to collect in Fraction 4, from which they can be precipitated with oxalic acid.

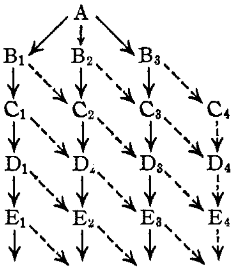

Fig. 1.

Results

The progress of the fractionation was followed in most cases by the absorption spectra as revealed by the direct vision spectroscope. Usually variations in the intensities of the absorption bands were considerable and left no doubt as to the order of precipitation of the members of the rare earth group. In the case of europium the absorption spectrum was photographed. This was thought to be necessary because its scarcity makes its detection extremely difficult in spite of the fact that it has a persistent line at about 5250 Å. Urbain and Lacombe[9] estimated from their work in isolating europium from monazite sand that its concentration in this material was 0.002%. On this basis the entire 20 kg. of cerium-free oxide used in this investigation contained approximately one gram of europium.

In order to follow the concentration of gadolinium, which has no absorption bands in the visible spectrum, the magnetic balance was used. This instrument was designed and built by Dr. F. H. Driggs.[10] It gives dependable relative values and works with remarkable rapidity. When it became necessary to estimate gadolinium in the presence of neodymium or samarium, the latter elements were estimated directly by the spectroscope, comparing with standard solutions and the gadolinium content calculated by difference.

The results obtained with our modified sodium nitrite precipitation agree with the usual order of basicity in Zones 1 and 3. In Zone 2 the order of decreasing basicity is found to be samarium, europium and gadolinium.

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(9) Urbain and Lacombe, *Compt. rend.*, **138**, 627 (1898).

(10) Driggs, THIS JOURNAL, **47**, 366 (1925).

The differences in basicity between these three elements are very slight and careful work was necessary to establish any differences at all. The separation of these three elements by any method which depends upon their basicities seems to be impracticable.

If scandium, yttrium and cerium are omitted, the order of decreasing basicity is the same as the order of increasing atomic number throughout the entire rare earth group. Because of the scarcity of illinium its relative basicity is made the subject of a separate paper which follows this one.

Summary

1. The sodium nitrite method of precipitating the rare earths has been modified in such a manner as to emphasize the differences in basicity which are found in the rare earth group. The efficiency of this method for fractionation has been greatly increased.

2. The order of decreasing basicity of the members of the rare earth group is identical with the order of increasing atomic number; the elements scandium, yttrium, cerium and illinium are not included in the present study.

3. While we have shown that samarium is more basic than europium and that europium is more basic than gadolinium, these differences are extremely slight, which accounts for the contradictory statements regarding these elements.

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Observations on the Rare Earths. XXXIIIa. The Basicity of Illinium and Yttrium

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The preceding paper[1] reports the basicity of the more common rare earths whose presence may be established by the usual methods. The object of this work was to determine the basicity of illinium and yttrium and thus complete the list of basicities of all the members of the rare earth group.

Material and Methods

The material was derived from two sources. The first quantity was prepared from the monazite residues of the gas mantle industry. It originally consisted of practically all the rare earth content of monazite sand after the removal of thorium. These residues were dissolved in acid and the cerium removed as completely as possible by precipitation with sodium phosphate.[2] After filtering the ceric phosphate, there was obtained a solution composed mostly of the salts of lanthanum, praseodymium, neodymium, illinium,

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[1] Sherwood and Hopkins, THIS JOURNAL, **55**, 3117 (1933).

[2] Neckers and Kremers, *ibid.*, **50**, 955 (1928).