[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

CESIUM SULFATE AS A CONFIRMATORY REAGENT IN THE DETECTION OF ALUMINUM

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Cesium salts, because of their unique properties, have long been used as reagents in micro-analytical work and with the increasing demand for salts of this element together with the opening of new ore deposits, it seems certain that much more general use of its interesting properties will result both in qualitative and quantitative analysis.

The familiar aluminum tests which depend on the formation of "Thenard's Blue" or "lakes" with organic dyes are not altogether satisfactory, especially for the average student in qualitative analysis. The formation of a relatively copious precipitate of the insoluble cesium alum, $Cs_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$, which contains only 4.75% by weight of aluminum, is on the other hand a simple and decisive test. Its sensitivity will be appreciated when it is recalled that a saturated solution of cesium alum at 0° is 0.00745 *M* with respect to aluminum ion, and that at 16° this value is but slightly greater, 0.0077 *M*. Concentrations of aluminum down to 0.1 mg. per cc. are easily and rapidly detected.

Procedure

The supposed aluminum hydroxide, separated in the usual manner from the other Group III metals, is dissolved in 1–5 cc. of hot 3 *M* sulfuric acid by repeatedly pouring the acid through the filter. (If the precipitate is large, it is more convenient to remove some of it and dissolve in an evaporating dish.) The resulting aluminum sulfate solution is cooled and 0.5–1 cc. of approximately 0.25 *M* cesium sulfate is added. On scratching the walls of the test-tube with a stirring rod, the dense white cesium alum separates and rapidly settles.

Time Required for Precipitation.—Due to the great tendency of cesium alum solutions to remain supersaturated, the following rough classification has been made

Concn. of Al ion in mg. per cc.	5 and greater	1–5	0.1–1
Time for precipitation	instantaneous	1 minute	3 minutes

Interfering Elements.—Although cesium has a great tendency to form double salts with many elements, only bismuth is likely to be troublesome. In practice this possibility of confusion may be eliminated by adding one drop of concd. hydrochloric acid to a portion of the white precipitate. Warm and add 1 cc. of hydrogen sulfide water. A brown precipitate of bismuth sulfide will indicate the presence of that element. Ferric and chromic alums are much more soluble than the aluminum alum. Beryllium and magnesium do not interfere. The elements lanthanum cerium, praseodymium, neodymium, erbium, yttrium, thorium, zirconium (and probably hafnium) form more soluble double cesium sulfates or form them much more slowly than aluminum.

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[Contribution from the Chemical Laboratory of the University of California]

AN OXIDE OF IODINE, I_2O_2. AN INTERMEDIATE COMPOUND

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The recent experimental proof by Abel and Hilferding[1] that the reaction between iodate and iodide ions in acid solution, long known as a fifth order reaction,[2] is of the fourth order at a low iodide concentration, has led me to reëxamine the series of investigations of Skrabal[3] on the rate of formation of iodate and iodide from iodine and hydroxide ion. Skrabal presented strong evidence that HI_3O and $I_3O_2^-$ exist as intermediate compounds in this reaction, and that HI_3O is a loose addition compound of iodine and hypoiodous acid. He also pictured $I_3O_2^-$ as a similar compound of iodine and iodite ion. The present analysis has led to the conclusion that $H_2I_2O_3$ and I_2O_2 also exist as intermediate compounds, and that $I_3O_2^-$ is really an addition compound of I_2O_2 and iodide ion.

Skrabal succeeded in demonstrating that the results of his rate measurements could be represented by three rate laws, A, B and C, and postulated the following mechanisms

	Relatively rapid equilibrium	$2IOH + I^- \rightleftharpoons I_3OH + OH^-$	(1a)
A	Rate-determining step	$I_3OH \longrightarrow$	(2)
	Main reaction	$3IOH + 3OH^- = 2I^- + IO_3^- + 3H_2O$	
	Relatively rapid equilibrium	$2I_3^- + OH^- \rightleftharpoons I_3OH + 3I^-$	(1b)
B	Rate-determining step	$I_3OH \longrightarrow$	(2)
	Main reaction	$3I_3^- + 6OH^- = IO_3^- + 8I^- + 3H_2O$	
	Relatively rapid equilibrium	$3I_3^- + 4OH^- \rightleftharpoons I_3O_2^- + 6I^- + 2H_2O$	(3b)
C	Rate-determining step	$I_3O_2^- \longrightarrow$	(4)
	4 + rapid steps	$I_3O_2^- + 2OH^- = IO_3^- + 2I^- + H_2O$	(5)
	Main reaction (Sum)	$3I_3^- + 6OH^- = IO_3^- + 8I^- + 3H_2O$	(6)

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[1] Abel and Hilferding, *Z. physik. Chem.*, **136**, 186 (1928).

[2] (a) Dushman, *J. Phys. Chem.*, **8**, 453 (1904); (b) Skrabal, *Z. Elektrochem.*, **28**, 224 (1922); **30**, 109 (1924); (c) Abel and Stadler, *Z. physik. Chem.*, **122**, 49 (1926).

[3] Skrabal, (a) *Monatsh.*, **32**, 815–903 (1911); (b) *Oesterr. Chem.-Ztg*, No. 11 (1913); (a) is the fifth paper of a series of twelve, 1907–1916, on hypohalous acids and hypophalites, and (b) is a general discussion of the stoichiometric reactions of iodine isolated and studied in his investigations.