V. E. Plyushchev, S. B. Stepina, B. D. Stepin, and L. I. Lepeshkova

1962

SovietRxiv

Abstract

Full Text

Chemistry

V. E. Plyushchev, S. B. Stepina, B. D. Stepin, and L. I. Lepeshkova

Heterotripolyhalides of Alkali Elements Similar in Properties and Their Significance for Obtaining Pure Rubidium and Cesium Compounds

(Presented by Academician I. V. Tananaev, 13 XII 1961)

Among the alkali elements similar in properties, rubidium and cesium are of the greatest interest, having found important applications in many fields of technology ([1-4]). Further identification of the specific properties of these rare elements and, consequently, the discovery of new areas of their application are being hindered by the absence of a simple industrial method for obtaining pure rubidium and cesium compounds practically free of impurities of the other alkali elements. In solving the problem of obtaining pure rubidium and cesium compounds, the greatest difficulty is the separation of the pairs K—Rb (K—microcomponent) and Rb—Cs (microcomponent—Rb or Cs), especially the former. The method of fractional crystallization ([1, 5]), the use of heteropoly acids ([1, 6]), and ion exchange ([7]) do not give the desired results, while extraction processes as applied to the separation of rubidium and cesium and to the purification of their compounds are only beginning to be studied.

The main obstacle to removing a microcomponent from rubidium or cesium salts is isomorphous cocrystallization, which in the compounds previously used for separation could not be eliminated. In selecting such compounds, the fact has until now been completely disregarded that the polarization of ions has a great influence on isomorphous crystallization. If the degree of polarization is different, then even when the ionic radii are equal, the formation of isomorphous mixtures can be avoided. Polarizability (deformability) and the polarizing ability of elements, as is known, generally have a very substantial effect on their chemical behavior, in particular on the stability of their compounds. As for the alkali elements similar in properties, among the few most differing physical characteristics of potassium, rubidium, and cesium, one of the foremost places belongs precisely to the polarizability of their ions (polarizability coefficient: K 0.87, Rb 1.87, Cs 2.79). In this connection, the study of compounds in which the mutual polarization of ions is especially large is of great interest.

In this respect, among various complex compounds, polyiodide compounds of alkali-metal halides (polyhalides) undoubtedly stand out. They have a neutral, nonpolar, but readily polarizable addend and a readily deformable complex-forming ion (most often iodine). Under these conditions the cation, located in

the outer sphere, can by its counterpolarization determine the stability of the entire molecule as a whole ([8]). Polyhalides are a special and very interesting group of complex compounds. Many compounds of this series were obtained as early as the last century ([9-11]), although there is still no consensus regarding the existence of some of them in the solid state or their molecular composition. According to the number of halogen atoms in the molecules of the compounds, it has been proposed to divide polyhalides into penta- and trihalides. Penta-compounds, for example $MeFJCl_3$ and $MeJCl_4$, have been little studied ([11-15]); however, it is known that an acceptable yield of these compounds can be achieved only by dry methods of synthesis ([12, 13, 15]), which do not—

of the products of hydrolysis ([12]). But such methods are not suitable for purposes of separation.

Trihalides form ([9]) a consecutive series in which the stability of the compounds increases with increasing atomic weight of the constituent halogens. In this case, salts containing iodine as the heaviest halogen form one series with respect to stability and crystalline structure, while compounds containing bromine form another. The compounds of the iodine series (CsJ_3, $CsBrJ_2$, $CsBr_2J$, CsClBrJ and $CsCl_2J$) are generally more stable than the bromine series ($CsBr_3$, $CsClBr_2$, $CsCl_2Br$), which is in good agreement with ideas about the crystal lattice of polyhalides, in which the heaviest halogen atom (J or Br) is located at the center of the cell. At the same time, the polyhalides of rubidium or potassium are less stable than the corresponding cesium compounds. Ephraim ([16]) also subdivides the polyhalides into iodine- and bromine-containing ones, proceeding from their stability, characterized by the ratio of the dissociation temperature of the most stable member of a given class (triiodide) to the dissociation temperature of the given compound. He showed that as long as a compound contains iodine, its stability does not differ greatly from the stability of the triiodide. Since the three halogen atoms contained in the polyhalides of alkali elements may by their nature be either identical or different, it seems to us more appropriate to subdivide polyhalides with three halogen atoms into isotri-polyhalides and heterotri-polyhalides.

If the latter are considered, then in them the ions J^-, Br^-, and Cl^-, with a sufficiently large radius, act as complex-formers and ligands. In this case the polarizing action of the cation will have an especially strong effect on the weakening of the covalent bond of the central atom with the ligands. And although the magnitudes of the polarizing action of cations on particular complex anions are unknown, and the choice of compounds for the separation of alkali elements similar in properties remains for the time being purely empirical, it is possible to use the difference in stability of heterotri-polyhalides to solve the problem of removing microimpurities coprecipitating with rubidium and cesium salts.

Until recently, among the heterotri-polyhalides only readily soluble compounds of the type $MeCl_2J$ had been used; these can be recrystallized from aqueous ([9,10,17]) or hydrochloric-acid solutions on cooling. Thus, Wells ([18]) long ago recommended, for obtaining pure CsCl, recrystallization of $CsCl_2J$ from hot HCl

(1 : 1), followed by ignition of $CsCl_2J$ to CsCl. An improvement of the method carried out in our time ([19]) makes it possible, after seven recrystallizations of $CsCl_2J$, to obtain cesium chloride of 99.9% purity and with a yield of 70%. For purification of rubidium salts from potassium, a compound of the same type, $RbCl_2J$, has been recommended ([20]). It is possible that similar results could have been achieved by using recrystallization from aqueous-alcoholic solutions of compounds of the type $MeBr_2J$. However, rubidium and cesium salts obtained on the basis of dichloro- and dibromoiodides cannot possess the purity required for a number of fields of application, since when $MeCl_2J$ or $MeBr_2J$ is used, ordinary co-crystallization of identical potassium, rubidium, and cesium compounds is inevitable.

For obtaining especially pure rubidium compounds, the decisive point is overcoming the most difficult problem of removing from them microimpurity potassium. In choosing ways to solve this problem, we drew attention to the circumstance that, in contrast to the compounds $MeCl_2J$ and $MeBr_2J$, for the other four known types of alkali-element heterotri-polyhalides ($MeCl_2Br$, $MeClBr_2$, MeClBrJ, and $MeBrJ_2$), no one has succeeded in obtaining potassium compounds ([9,10,12,21,22]), which is evidently connected with the presence of strong counterpolarization on the part of K^+, leading to destruction of the complex anions $ClBrJ^-$, Cl_2Br^-, $ClBr_2^-$ (still less stable, and probably not existing even in solution, are many trihalides of lithium and sodium). Evidently, for the same reasons it was not possible ([10],

[12, 21]) to isolate from solution also $RbBrJ_2$. Taking into account that the compounds $RbCl_2Br$ and $RbClBr_2$ are unstable in aqueous solutions[9, 10, 17], we[23] investigated certain properties and the conditions for the isolation of rubidium chlorobromoiodate, $Rb[J(ClBr)]$, the most stable of all the other rubidium heterotripolyhalides, for which analogous potassium compounds are unknown. As a result, a method was developed for purifying rubidium from potassium[24], the further improvement of which[25] made it possible to obtain, from technical $RbCl$ (2-3% potassium), especially pure rubidium preparations containing only 0.0002% potassium. By this method $RbCl$ is twice converted at 90° into $Rb[J(ClBr)] \cdot H_2O$, first in aqueous solution and then in a 0.5 M solution of CH_3COOH, with intermediate calcination of the compound at 400°. None of the methods hitherto recommended for purifying rubidium salts from micro-impurities of potassium has ensured the preparation of rubidium preparations of such high purity. Along with high efficiency, purification of rubidium salts through $Rb[J(ClBr)] \cdot H_2O$ is characterized by simplicity and economy.

The development of methods for obtaining pure cesium compounds has hitherto been limited by the absence of a reliable means of removing micro-impurities of rubidium. The method proposed by us[26] is based on precipitation from aqueous-alcoholic solutions of the complex compound—cesium diiodobromide ($CsBrJ_2$)—the only compound with the anion BrJ_2^- known for the alkali elements[10, 12, 21], which is of primary importance for separating cesium from

a mixture of salts. (All the other types of heterotripolyhalides are known both for rubidium and for cesium.)

The essence of the method is as follows: to an aqueous-alcoholic solution of $CsBr$* heated to 70–80°, containing water, alcohol, and $CsBr$ in a weight ratio of 2 : 2 : 1, 1.2 parts by weight of finely ground elemental iodine are added.

Table 1

Change in the content of impurities (wt. %) of alkali elements in cesium bromide

Initial $CsBr$				$CsBr$ after the first precipitation of $CsBrJ_2$				$CsBr$ after the second precipitation of $CsBrJ_2$			
Li	Na	K	Rb	Li	Na	K	Rb	Li	Na	K	Rb
–	–	0.04	0.15	–	–	0.019	0.027	–	–	0.009	0.019
–	–	0.04	0.30	–	–	0.019	0.020	–	–	–	–
–	–	–	1.0	–	–	–	0.08	–	–	–	0.010
0.002	0.043	1.00	2.4	–	–	0.024	0.10	–	–	0.008	0.024
0.002	0.043	1.00	2.4	0.002	<0.004	0.028	0.11	<0.002	0.002	0.004	0.020
0.002	0.043	1.00	2.4	0.002	<0.004	0.021	0.11	<0.002	0.002	0.006	0.026
0.002	0.043	1.00	2.4	0.002	0.004	0.007	0.10	<0.002	0.003	0.004	0.020
–	–	–	5.0	–	–	–	0.52	–	–	–	0.026

Note. The weighed portions of the initial $CsBr$ were 10–20 g; impurities were determined by flame photometry.

The solution is cooled with ice, with vigorous stirring, to +5°. The $CsBrJ_2$ crystals that separate on cooling (the onset of crystal separation is at +20°) are filtered off and calcined. To avoid fusion, calcination is carried out in two stages: at 150° to remove the main portion of iodine, and then at 400° for its final removal. The $CsBr$ obtained after calcination is subjected to a repeated treatment analogous to that described above. Cesium bromide after the second precipitation contains 0.02% rubidium, not more than 0.005% K, 0.002% Na, and 0.002% Li (content of the principal substance–99.95%), when the initial $CsBr$ contains 5% rubidium and up to 1.5% other alkali elements (see Table 1).

At each precipitation, ~60% of the $CsBr$ passes into the precipitate. The cesium bromide remaining in the mother liquors and enriched with impurities is recovered by evaporating the solution and subsequent calcination, and is again introduced into the process.

* The starting compounds subject to purification may be any other cesium salts whose conversion into $CsBr$ can readily be effected through the tetraoxalate^(27)—carbonate.

Thus the losses of the most expensive component (CsBr) are reduced to a minimum. The iodine removed during calcination can be trapped by one of the methods known in the literature and thus completely regenerated. All this makes it possible to organize the production of very pure cesium salts from a technical product at a price exceeding the cost of the latter by no more than 10%.

The advantages of the new method are: 1) a high purification factor (10–20); 2) selectivity of extraction of CsBr from a mixture with other alkali elements, which is not achieved by any of the previously described methods; 3) exclusion from the purification process of any additional operations, since nonvolatile ions are not introduced into the process.

Thus, heterotripolyhalides of alkali elements close in their properties prove to be very promising compounds for removing potassium microimpurities from rubidium salts and for obtaining cesium compounds practically free from impurities of other alkali elements.

Moscow Institute of Fine
Chemical Technology
named after M. V. Lomonosov

Received
6 XII 1961

CITED LITERATURE

1. V. E. Plyushchev, I. V. Shakhno, *Usp. khim.*, **26**, 944 (1957).

2. F. M. Perelman, *Rubidium and Cesium. A List of Established and Possible Fields of Application*, Moscow, 1959.

3. F. M. Perelman, *Rubidium and Cesium*, Publishing House of the Academy of Sciences of the USSR, 1960.

4. B. D. Stepin, *Khim. prom.*, No. 4, 64 (1959).

5. B. D. Stepin, V. E. Plyushchev, *ZhNKh*, **6**, 462 (1961).

6. W. Geilman, W. Gebauhr, *Zs. anal. Chem.*, **142**, 241 (1954).

7. B. D. Stepin, A. M. Tartakovskaya, V. E. Plyushchev, *ZhNKh*, **5**, 1612 (1960).

8. Ya. A. Fialkov, *Interhalogen Compounds*, Kiev, 1958.

9. H. L. Wells, S. L. Penfield, *Am. J. Sci.*, **43**, 475 (1892).

10. H. L. Wells, S. L. Penfield, H. L. Wheeler, *Am. J. Sci.*, **43**, 17 (1892).

11. H. L. Wells, H. L. Wheeler, S. L. Penfield, *Am. J. Sci.*, **44**, 42 (1892).

12. H. W. Cremer, D. R. Duncan, *J. Chem. Soc.*, **1931**, 1857.

13. F. Filhol, *J. Pharm.*, **25**, 431 (1839).

14. W. N. Rae, *J. Chem. Soc.*, **107**, 1286 (1915).

15. W. N. Rae, *J. Chem. Soc.*, **113**, 880 (1918).

16. F. Ephraim, *Ber.*, **50**, 1069 (1917).

17. F. L. Gilbert, R. R. Goldstein, T. M. Lowry, *J. Chem. Soc.*, **1931**, 1094.

18. H. L. Wells, *Am. Chem. J.*, **26**, 268 (1901).

19. M. Ischibaschi, T. Jamamoto, T. Hara, *Bull. Inst. Chem. Res. Kyoto Univ.*, **37**, No. 2, 145 (1959).

20. M. Ischibaschi, T. Jamamoto, T. Hara, *Bull. Inst. Chem. Res. Kyoto Univ.*, **37**, No. 3, 153 (1959).

21. H. W. Foote, M. Fleischer, *J. Phys. Chem.*, **44**, 640 (1940).

22. H. W. Cremer, D. R. Duncan, *J. Chem. Soc.*, **1932**, 2032.

23. B. D. Stepin, V. E. Plyushchev, *ZhNKh*, **6**, 2187 (1961).

24. V. E. Plyushchev, B. D. Stepin, USSR Author' s Certificate No. 132627 (1960).

25. B. D. Stepin, V. E. Plyushchev, USSR Author' s Certificate No. 140051 (1961).

26. S. B. Stepin, B. D. Stepin, L. I. Lepeshkova, V. E. Plyushchev, USSR

Author' s Certificate No. 138927 (1961).

27. A. Suetuna, *Bull. Chem. Soc. Japan*, **25**, 248 (1952).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.