AN IMPROVED METHOD OF PREPARATION OF POTASSIUM CYANIDE-^{14}C

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SUMMARY

A safe procedure for the conversion of barium carbonate-^{14}C to potassium cyanide-^{14}C on a 6-7 mmol scale in 90-98% yield was developed. Barium carbonate-^{14}C was heated with excess potassium azide in a matrix of sand without added potassium metal, allowing safe, rapid and convenient recovery of the cyanide.

Key Word: Potassium Cyanide-^{14}C

INTRODUCTION

A variety of methods are known for the conversion of barium carbonate-^{14}C to potassium cyanide-^{14}C, (1) a useful intermediate for many labelling syntheses. For many years we have used one of these (Method III) (2), the reaction of barium carbonate-^{14}C with potassium azide in an excess of molten potassium at about 700° under argon, to prepare potassium cyanide-^{14}C in about 85% yield, but the method is limited to a scale of 1 mmole and the work-up procedure is tedious, time-consuming, and potentially hazardous due to the excess potassium.

With regard to the other methods presented by Murray and Williams (1), Methods I and IV also involve an excess of potassium metal. Method V requires several steps and affords cyanide in only about 75% yield. Method VI is useful for large scale preparations (as high as 90 mmoles (3)), but it involves five steps and offers only about 76% overall yield of cyanide. Jeanes' method

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(Method II) is an improved modification of that of McCarter (4), but it suffers from the inconvenience of requiring a gas train and requires four hours of heating at 650°.

Of the methods reported since publication of Murray and William's book, several (5-7) are variations of Jeanes' procedure. A more recent patented process by Banfi and coworkers (8) claims quantitative yields of cyanide but requires the use of a gas train, very high temperatures (1000-1100°) and catalysts to produce hydrogen cyanide.

We report here several approaches to the conversion of barium carbonate to potassium cyanide culminating in a variation of the original procedure of Adamson (9) which is rapid, convenient, allows at least a 6-fold increase in scale and avoids the necessity of decomposing a large amount of potassium. Earlier modifications of this method (10) were designed to avoid explosions and to give more consistent yields, but yields of cyanide ranged from 60-85%.

Our first approach, in which the original procedure (2) was modified by distillation of the potassium out of the reaction tube under high vacuum, allowed safe, fast and easy recovery of the cyanide, but presented a new set of difficulties in the distillation of the metal. However, the yield of cyanide was good (90%).

One attempt to convert barium cyanamide, which can be prepared easily in almost quantitative yield, (11) to cyanide by treatment with sodium at 650° afforded cyanide in 44% yield, but the work-up was complicated by a large amount of water-insoluble material. Vercier (12) has carried out this process successfully in three stages by using a higher temperature (800°) for the decomposition of the intermediate sodium cyanamide.

Finally, based on the fact that sodium azide on heating decomposes to nitrogen and sodium, a series of experiments in which barium carbonate was heated under an atmosphere of nitrogen with potassium azide without additional potassium

led to a simple, rapid, and almost quantitative preparation of cyanide. (Note: It is important to carry out this reaction under nitrogen. When argon was used the yield of cyanide was reduced to about 60%).

Barium carbonate and potassium azide in molar ratio of about 1:7.3 were mixed with sea sand (the amount depending on the scale of the reaction) in a Vycor or quartz tube and the mixture was heated very slowly under nitrogen. The optimum time-temperature schedule must be determined for the particular apparatus used and the scale of the reaction (see Table 1). Work-up involves merely the addition of water to the cooled reaction mixture and filtering to obtain an aqueous solution of potassium cyanide, which is then further processed as required (1).

Using this method, the yield of cyanide (by titration) was 83-100% in a series of experiments using unlabelled barium carbonate (Expts. 3,4 and 7). Using barium carbonate-^{14}C on a 6-mmol scale, potassium cyanide-^{14}C was obtained in 90-98% yield (Expts. 8 and 9).

EXPERIMENTAL

General Procedure: The barium carbonate and potassium azide were thoroughly mixed in a Vycor or quartz tube approximately 25 mm. in diameter, then clean sea sand (1-6 times the volume of the barium carbonate-potassium azide mixture) was added and thoroughly mixed. Then an additional layer of sand (approximately 2 cm) was added, and under an atmosphere of nitrogen, the tube was heated carefully in a tube furnace to about 350°, then very slowly through the range 350-450°, so that evolution of nitrogen did not become so vigorous that potassium vapor was expelled from the heated reaction zone. When gas evolution subsided, the temperature was raised to 700° for 10-30 min. to complete the reaction.

After cooling to room temperature, the reaction mixture was triturated with water, filtered, and the residue thoroughly extracted with water

Table 1

Expt.	$BaCO_3$ (mmol)	KN_3 (mmol)	Sand (vol[a])	Time Schedule	% Yield of Cyanide[b]
1	1.00	7.0	1	350° for 2 hrs	0
2	1.00	7.0	1	350° for 2 hrs, 500° for 30 min	60
3	1.00	7.4	1	To 360° over 30 min, slowly to 400°, then 600° for 20 min	100
4	3.00	22.2	3	To 370° over 1 hr, slowly to 400° (vigorous reaction at 380-400°), then to 680° over 20 min, and 680° for 10 min	94
5	6.00	44.4	1	To 360° over 30 min, to 440° over 20 min (lost K vapor at about 380° by vigorous reaction) then 620° for 30 min	60
6	6.00	44.4	2	To 360° over 30 min, at 450° reaction became vigorous and K was lost - reaction discontinued	--
7a	6.00	44.4	4	25° to 320° over 20 min, slowly to 360°, held at 360° until gas evolution stopped then slowly to 450°, then 700° for 10 min	83
7b	6.00	44.4	4	(repeat of 7a)	85
	$Ba^{14}CO_3$ mmol				
8	6.25	45.0	6	To 385° over 1 hr, then to 420° over 15 min (vigorous release of gas), then gradually to 480°, finally to 700° for 15 min	98
9	6.66	48.6	6	To 430° over 80 min (gas evolution began), then slowly to 480°, then rapidly to 700° over 30 min	90

a) 1 vol = approx. volume of $BaCO_3$-KN_3 mixture.

b) Determined by titration of alkaline aqueous filtrates (13).

which was also filtered. The yield of cyanide was determined by titration of the combined filtrates with silver nitrate in the presence of excess ammonium hydroxide and a small amount of potassium iodide (13). Table 1 summarizes the experiments, in which various amounts of sand and various temperature schedules were used on different scales. In general, as the scale is increased, the proportion of sand should be increased and the temperature should be raised more cautiously in the range 350-450°. Final heating to 600° or higher seems to be required for high yields of cyanide (compare experiments 1-3).

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