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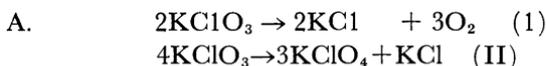
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Radiochlorine³⁶ as a Tracer in the Decomposition of Potassium Chlorate

By F. E. BROWN AND J. D. WOODS

INTRODUCTION

The thermal decomposition of potassium chlorate has been shown to be complex. Oxygen is evolved and, depending upon the conditions, various quantities of perchlorate are formed. At least two sets of equations have been proposed to explain the reaction. Otto and Fry (5) proposed that potassium chlorate decomposes by two simultaneous reactions.



In a more recent publication Glasner and Weidenfeld (2, 3), on the basis of kinetic data, suggested that reactions I and II are not simultaneous. Rather, they proposed that two consecutive reactions occur whereby atomic oxygen adds to chloride.



A study was initiated to determine, if possible, which type of decomposition is correct. If proposal B is correct, a mixture of chlorate and radioactive chloride should yield radioactive perchlorate on decomposition.

While this study was in progress, Vanden Bosch and Aten (7) published a note reporting results of a similar study. They decomposed sodium chlorate in the presence of sodium chloride containing Cl³⁴ and Cl³⁸. They found negligible activity in the perchlorate, thus disproving the proposal of Glasner and Weidenfeld.

In this study potassium chlorate and potassium chloride were used. Chlorine³⁶ was the radioactive tracer.

PREPARATION OF KCl³⁶

The Cl³⁶ was obtained as 1.4N HCl³⁶ with a specific activity of 0.23 mc/g., or 5.1×10^8 disintegrations per second. One tenth milliliter of this HCl³⁶ was added to 0.0300 g. of KCl in a small pyrex test tube. The tube was placed in a closed system and distilled until the KCl residue was dry. Excess HCl³⁶ was recovered. Since a rapid isotopic exchange occurs between HCl and KCl, the result-

ing KCl contained considerable activity. A sample was counted and found to have a relative activity of 9,296 counts per minute per milligram of chlorine (Sample 1, Tables I and II).

PRELIMINARY EXPERIMENTS

Preliminary experiments revealed that when a mixture of 0.2000 g. of KClO_3 and 0.0250 g. of KCl is heated at 510°C . for 60 minutes a good yield of perchlorate is obtained in the residue. This is in accord with data reported by Glasner and Weidenfeld (2). When analyzed by standard methods (1, 4) the residue from a preliminary experiment was found to contain 0.0725 g. of KCl, 0.0280 g. KClO_3 , and 0.099 g. of KClO_4 . Further preliminary experiments showed that it was possible to isolate the chloride from each of these compounds.

PROCEDURE

A mixture of 0.2000 g. of KClO_3 and 0.0182 g. KCl^{36} were heated at 510°C . for 62 minutes in a pyrex test tube extending into a vertical electric furnace. The residue was dissolved and the chloride was precipitated with excess silver nitrate. The precipitate was filtered on a weighed filter paper, washed, dried, and weighed according to standard methods (6). This precipitate is Sample 2, Tables I and II.

Ordinary KCl was added to the filtrate and previous wash water. The chloride was precipitated and weighed (Sample 3, Tables I and II). This was done to remove last traces of Chloride³⁶ from the solution. Still a second quantity of ordinary KCl was added to the filtrate, filtered and weighed (Sample 4, Tables I and II).

The filtrate was then evaporated to approximately 60 ml. and tank SO_2 was bubbled into the solution to reduce the chlorate to chloride (4). The resulting chloride was precipitated with silver nitrate, filtered, washed and weighed (Sample 5, Tables I and II).

Another final quantity of wash KCl was added to the filtrate, precipitated as AgCl , and weighed (Sample 6, Tables I and II). Finally the filtrate, containing only perchlorate, was evaporated to about 1 ml. Two ml. of ice water was added and the KClO_4 was filtered on a weighed filter paper, washed twice with cold water, twice with cold ether, and was weighed (Sample 7, Tables I and II). All samples were dried at 110°C . for one hour before weighing.

The radioactivity of these samples was determined by a 2C32 counter tube in an S-20 tube housing. The scaler was a Model 161, S-295 capable of counting 10,000 counts per minute.

The counter housing contained four shelves at different distances from the counter tube. Sample 3 was counted on both shelf 1 and 3 to find the shelf factor. Thus, samples of activity greater than 10,000 c/m could be counted on shelf 3 and its activity on shelf 1 could be calculated by multiplying by the shelf factor.

RESULTS

The results of this experiment are summarized in Tables I and II. Table 1 records the details of the counting of samples. The second column lists the number of times each sample was counted, and the third column shows the duration of each counting period (Δt). Column 4 refers to the shelf on which the samples were placed in the counter tube housing. Column 5 shows the average counts per minute for each sample, and Column 6 the background count for the empty housing.

Table II lists the weight of AgCl samples and the source of the chloride. (Sample 7 was weighed directly as KClO_4). The fourth column shows the calculated weight of Cl in each sample. Column 5 lists the shelf factor used to calculate the activity of the samples to activity on shelf 1. The sixth column shows the activity of the samples, and the last column lists the calculated specific activity in counts per minute per milligram of Cl.

Sample 1 showed a specific activity of 9,296 c/m per milligram of Cl for the KCl^{36} . Sample 2, containing the chloride from the reaction mixture, had so much activity that its count was calculated by difference to contain approximately 155,000 c/m, a specific activity of 5,720 c/m per milligram of Cl. Sample 3 contained a specific activity of 10.1 c/m, an activity that one could expect to remain from Sample 2 due to the slight solubility of AgCl. The remaining samples contained relatively small specific activities.

Table I.
Details of Counting

Sample	Times Counted	Δt .	Shelf	c/m	BG
1	6	2 min.	3	3356.3	30.2
2	1		(calculated)		
3	2	30 min.	1	294.2	30.2
3	2	30 min.	3	84.3	24.7
4	2	30 min.	1	46.8	24.6
5	2	30 min.	1	36.2	30.2
6	2	30 min.	1	29.9	30.2
7	3	30 min.	1	42.5	30.2

Table II.

Results

Sample	Wt. AgCl. (milligrams)	Source	Wt. Cl. (calculated)	Shelf Factor (shelf 1)	c/m-BG. (shelf 1)	Sp. Act. (c/m per mg.)
1	6.3	KCl ³⁶	1.6	3.36	14,502	9,296
2	109.7	Chloride	27.1	1	155,000 ¹	5,720 ¹
3	104.5	Wash KCl	25.8	1	264	10.1
4	76.2	2nd Wash	18.8	1	22	1.2
5	14.0	KClO ₃	3.3	1	6	1.8
6	102.8	Wash KCl	25.4	1	-.3	-.0
7	48.2 ²	KClO ₄	12.3	1	13	1.1

¹Calculated value.²Weighed as KClO₄.

DISCUSSION OF RESULTS AND CONCLUSIONS

The total activity in counts per minute in the original reaction mixture was obtained by multiplying the specific activity of the KCl³⁶ (Sample 1) times the weight of KCl³⁶ in the chlorate-chloride mixture. This gave an activity of 9,296 c/m X 18.2 mg = 169,164 c/m per milligram.

In the original mixture (0.0182 g. KCl + 0.200 g. KClO₃) 13.01% of the total Cl was radioactive. The data also show that 18.5% of the total Cl ended up as perchlorate. If perchlorate were formed by the addition of oxygen to chloride, 13.01% X 18.5% = 2.41% of the activity could have been in the perchlorate. 2.41% of 169,164 = 4,177 c/m, corresponding to a specific activity of 339 c/m per milligram. The data (Table II, Column 7) show a specific activity of no more than 1.1 c/m per milligram in the perchlorate. Thus, these results refute the proposal that potassium perchlorate is formed by the addition of oxygen to chloride during the decomposition of chlorate.

The data also show (Table II, Column 7) that the chlorate contained a specific activity of only 1.8 c/m per milligram of Cl. This relatively small activity in both the chlorate and perchlorate leads to the further conclusion that chloride does not appreciably undergo isotopic exchange with chlorate or perchlorate at 510° C.

These conclusions are in agreement with those of Vanden Bosch and Aten (7).

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