Cesium Cobalt Dicarbollide—Solubility, Precipitation, and Reactivity in Basic Aqueous Solution

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CESIUM COBALTDICARBOLLIDE - SOLUBILITY, PRECIPITATION, AND REACTIVITY IN BASIC AQUEOUS SOLUTION

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Abstract - The title compound, $\text{Cs}^+[\text{Co}((3)-1,2-\text{C}_2\text{B}_{9}\text{H}_{11})_2]^-$ (CsCDC), was precipitated with a NaCDC solution from solutions containing CsCl. The reaction was followed by measuring the loss of light intensity as the precipitate formed. The $[\text{Cs}^+]$ and [CDC$^-$] at the point of precipitation were estimated and approximate values of the $K_{sp}$ for CsCDC determined at room temperature: $8 \times 10^{-6}$ (water), $7 \times 10^{-6}$ (1 M NaOH), and $2 \times 10^{-6}$ (5 M NaCl/0.1 M KOH/1.0 M NaOH). In some cases, NaCDC precipitated from solution when added to the latter salt solution. For the medium, 5 M NaNO$_3$/0.1 M KOH/1.0 M NaOH, a four-fold excess of NaCDC was added to a 10mM Cs$^+$ solution at 40$^\circ$C and the [CDC$^-$] measured spectrophotometrically. Only CsCDC precipitated, and a $K_{sp}$ of $3.9 \times 10^{-6}$ was determined. The solubilities of CsCDC were measured in NaNO$_3$ and NaCl solutions at 30$^\circ$C as a function of the Na salt concentration. The reaction of the CDC$^-$ with OH$^-$ slowly produces B(OH)$_4^-$, H$_2$, and CoO(OH). The reaction of 22$\mu$M CsCDC with 1M NaOH has a first order rate constant at 56$^\circ$C of $8.8 \times 10^{-7}$ s$^{-1}$, while that for 14 mM NaCDC is $7.2 \times 10^{-7}$ s$^{-1}$. The activation energy for the reaction is 110 kJ.
The removal of radioactive $^{137}$Cs +1 ions from nuclear waste solution is a major environmental problem. The removal may be achieved by ion exchange, extraction or precipitation. Considerable information is available on the first two methods, but little attention has been given to precipitation, even though this is the method to be used to separate $^{137}$Cs from the approximately 121 million liters of nuclear waste at the Savannah River Site (SRS). The tetraphenylborate anion, $B(C_6H_5)_4^-$ (TPB$^-$), is scheduled to be the precipitating agent, but there may be other anions that should be considered since problems are associated with the use of TPB$^-$, one being the slow formation of environmentally harmful benzene through the breakdown of TPB by radiation. A possible Cs$^+$ precipitating agent is $[\text{Co((3)-1,2-C}_2\text{B}_9\text{H}_{11})_2]^{-}$ (CDC$^-\$). This boron cluster species with a $\pi$-bonded Co(III) ion recently has been pointed out to have many potential uses. It has been utilized on a large scale to extract Cs$^+$ from acidic aqueous solution into nitrobenzene. CsCDC has a solubility in water of 0.975 mM at 23°C while CsTPB has a solubility of 0.028 mM at 20°C. Even though CsCDC is more soluble than CsTPB, there is little possibility of forming environmentally harmful materials in waste processing, because no harmful volatiles are produced. The ability of CDC$^-$ to precipitate Cs$^+$ in aqueous solution and the solubility of CsCDC have been investigated and the results are reported here. Since the SRS waste is basic (pH=14) and concentrated in NaNO$_3$ (~5M), it is necessary for this study to incorporate these conditions.

Even though CDC$^-$ has been reported to "withstand boiling with 5 M non-oxidizing acids as well as with up to 30% alkali hydroxides for many hours without any change," it was necessary to investigate the stability of CDC$^-$ in base solution over long periods of time. This report examines the reaction of CDC$^-$, as CsCDC and NaCDC, with NaOH solutions in the absence and the presence of high [NO$_3^-$].

**EXPERIMENTAL**

**Chemicals**

CsCDC was obtained from Boron Biologicals, Inc. Raleigh, NC. A solution of NaCDC was prepared by passing a nearly saturated (ca. 0.9 mM) CsCDC solution over a cation exchange resin, which had been washed with a concentrated NaCl solution. The resulting solution, which was concentrated by boiling, had a [Cs$^+$] below the detection limit of the ion chromatograph. The CDC$^-$ has bands at 281($\lambda$ 35000) and 445 nm(\$ 420 M$^{-1}$cm$^{-1}$), both of which obey Beer's Law. The 445 nm peak obeys Beer's law in solutions with high [OH$^-$] and [NO$_3^-$]. NaOH was the source of hydroxide.
The Cs salt of hexabrominated CDC\(^-\) (CsBCDC), \(\text{Cs}^+\text{Co}((\text{C}_2\text{B}_9\text{H}_8\text{Br}_3)_2)^-\), was prepared by the procedure of Hawthorne et al.\(^9\) with a yield of 84% using CsCDC instead of RbCDC in the bromination reaction. The compound had a UV band at 295 nm (13,000 M\(^-1\) cm\(^-1\)). \(^{11}\)B NMR(acetone): \(\delta\) 6.0(singlet), 4.0, -1.3(singlet), -4.3, -16.8 and -23.0, with a relative area ratio 1:1:2:2:2:1, respectively.

**Instrumentation**

(a) A Shimadzu UV-3100 recording spectrophotometer was used to record the UV-visible spectra.
(b) \(^{11}\)B NMR spectra were obtained at 115.85 MHz with a Nicolet NT-360 spectrometer which was externally referenced to BF\(_3\)-OEt\(_2\). Positive shift values were downfield.
(c) A Dionex 2003i ion chromatography system was used to obtain the [Cs\(^+\)] of the solutions. A volume of 1 mL was injected into the instrument which had a 50mL sample loop and an IonPac CS-10 column. The eluent was a 4 mM 2,3-diaminopropionic acid monohydrochloride (Aldrich)/ 40 mM HCl solution. A flow rate of 1mL/min was used with suppressed conductivity being the detection mode. These are the approximate elution times (min): Na\(^+\), 2; K\(^+\), 3; and Cs\(^+\), 4. In order to detect 1 mM Cs\(^+\) or less, the [Na\(^+\)] and [K\(^+\)] had to be less than 50 mM. This placed a severe restriction on the use of ion chromatography since the detection limit of Cs\(^+\) was about 0.01 mM.
(d) A Gow-Mac 580 Gas Chromatograph with a Supelco 60/80 molecular sieve 5A column (3 ft x 1/8 in) was used to detect the presence of H\(_2\) and was operated under the following conditions: column, detector and injector temperatures, 23\(^\circ\)C; He flow rate, 60 mL/min; attenuation, 1X; and detector current, 250 mA.
(e) The black product obtained from the reaction of CDC\(^-\) with base was identified as Co(O)OH by Dr. William Pennington at Clemson University using a Scintag X-ray powder diffractometer.

**Typical precipitation experiment**

An solution (25 mL) of 10 mM CsCl was prepared using water or a given medium as solvent, and 2 mL were removed for the spectrophotometer reference. The precipitating agent (0.075 M NaCDC) was added in 0.1 mL increments to the stirring solution. After each increment was added, the solution was allowed to stir for five minutes before the %T of a 2 mL aliquot was measured at 600 nm using a B&L Spectronic 20. As the precipitate formed, the turbidity of the solution increased, and the %T decreased. This procedure
was continued until one equivalent of precipitating agent (3.1 mL) was added. When complete, the flask was sealed, and the solution allowed to stir for more than 24h. The solution was then filtered. The resulting solid was washed with cold water and dried in air at 110°C. The fraction of Cs precipitated in the experiment was determined from the mass of the CsCDC collected and the theoretical mass possible. The UV-visible spectrum of the solution and, if possible, the [Cs⁺] were measured.

**Solubility Measurements**

A saturated CsCDC solution with excess solid was prepared in a sealed flask. The mixture was placed into a temperature-controlled water bath with a shaker attachment. After several days of slow shaking, the solution was removed from the bath and the UV-visible spectrum of the filtered solution obtained. The [Cs⁺] in some solutions was measured using ion chromatography.

**Rate studies**

(a) Solid CsCDC, or an appropriate volume of NaCDC solution, was added to enough NaOH solution to obtain 50 mL of the desired [CDC⁻] and [OH⁻]. In some cases, solid NaNO₃ was added to produce a given [NO₃⁻]. The solution was placed in a shaking water bath at the required temperature and aliquots were removed at regular time intervals. They were cooled to room temperature and a UV-visible spectrum was taken of each. The absorbance (A) was measured at 281 nm, or if NO₃⁻ was present, at 445 nm. To obtain the first order rate constant (k) a plot was made of the ln(A) vs. the time the sample spent in the water bath.

(b) A solution of NaCDC (ca. 14mM) was prepared with 1.0M NaOH and the ¹¹B nmr spectrum measured at various times with the sample at 56°C. The area of the B(OH)₄⁻ peak (+1.52 ppm) was determined for each spectrum and the % of the total B present as CDC⁻ (P) calculated. The value of k was calculated from the plot of ln(P) vs. time.

**H₂ as a product**

The reaction was carried out three times on a vacuum line in order to detect and determine the amount of H₂ generated. The experiments used a 88.2 mL vessel containing 0.20 g of CsCDC and 25 mL of 1.0 M NaOH. The container was evacuated three times with a "freeze-thaw" procedure and sealed with a stopcock. After remaining
in a 65°C bath for several days, the solution was cooled to freezing temperature and the vessel opened to the manometer. The pressure of the gas in the vessel was measured, and a sample of the gas injected into a gc. The sample showed the presence of trace amounts of H₂, O₂ and N₂. Because of the small amount of H₂ produced, the gc could qualitatively detect the presence of H₂, but not give the amount produced. The moles of H₂ were calculated from the small pressure increase, assuming only H₂ was formed. The change in the [CDC⁻] may be made by measuring the UV-visible spectra or by using the rate equation. The moles of H₂ formed per mol of CDC⁻ decomposed were calculated to be 0.46, 0.29 and 0.26.

RESULTS AND DISCUSSION

Precipitation

The precipitation of Cs⁺ from solution with CDC⁻ was studied with a simple, relatively inexpensive turbidimetric analysis method. In this method the intensity of transmitted light through the solution (%T) is measured at a non-absorbing visible wavelength (600 nm) as the solution of the precipitating agent (NaCDC) is added. Unfortunately, this is not as sensitive as the nephelometric analysis method which measures the amount of light scattered at right angles to the light beam (Tyndall effect) as the precipitate forms. However, the equipment required for the turbidimetric method was more readily available. Furthermore, for this method, the precipitate needs to be one that settles relatively slowly. This is the case for the CsCDC precipitate.

As a solution of NaCDC is added slowly to a Cs⁺ solution, a bright yellow precipitate forms. Once the insoluble CsCDC appears, the %T of the solution begins to decrease and continues to decrease as more NaCDC is added. At the concentrations being used, a limiting value of the %T (<5%) is usually reached before the equivalence point. Fig. 1 shows the turbidity measurements for solutions of 10 mM CsCl with 0.075M NaCDC and 0.075M NaTPB in water. The CsTPB precipitation was carried out for comparison with CsCDC. The lower solubility of CsTPB can be observed from the larger amount of precipitating agent required to initiate precipitation of CsCDC.

The value of the Ksp for CsCDC may be obtained from the precipitation reaction in several ways. The incipient Ksp, (Ksp)in, is found from the turbidity curve (Fig. 1) by estimating the [Cs⁺] and [CDC⁻] at the point of incipient precipitation. The absorbance Ksp, (Ksp)ab, is found when some CDC⁻ is added and the absorbance of the CDC⁻ remaining in solution is measured. The [CDC⁻] and [Cs⁺] are calculated assuming only
CsCDC precipitates. A $K_{sp}$ based on the direct measurement of both concentrations, $(K_{sp})^{ac}$, is obtained if both the $[Cs^+]$ and $[CDC^-]$ can be measured by independent means. A $K_{sp}$ based on the mass of precipitate obtained, $(K_{sp})^{ma}$, was determined from the fraction of Cs precipitated from solution. Since an excess of reactant ions are required to initiate precipitation, the value of $(K_{sp})^{in}$ is expected to be larger than the other $K_{sp}$ values.

Precipitating $Cs^+$ from solutions with high salt concentrations limited the ways of obtaining the $K_{sp}$ value. The large $[Na^+]$ made it difficult to determine the $[Cs^+]$ by ion chromatography. Therefore, obtaining $(K_{sp})^{ac}$ in these solutions was difficult. It was also difficult to accurately obtain $(K_{sp})^{ma}$ since some of the precipitate was lost when it had to be washed free of salt contamination before it was dried and weighed.

Initial studies of CsCDC precipitation were carried out in a chloride medium (5M NaCl/0.1 M KOH/1.0 M NaOH). A nitrate medium (5M NaNO$_3$ / 0.1 M KOH / 1 M NaOH) would have been preferable since it is similar to the SRS waste medium. Unfortunately, the nitrate ion had an intense band in the ultraviolet which interfered with the more intense CDC$^-$ band making it impossible to measure low [CDC$^-$] in that medium. The room temperature results of precipitation experiments in water and in the chloride medium are summarized in Table 1. Some precipitation studies were made in the nitrate medium using the much weaker band at 445 nm for [CDC$^-$] measurements and these are described below.

In water, the precipitation of CsCDC gave a $K_{sp}$ of about $4 \times 10^{-6}$. With 10 mM Cs$^+$ in the chloride medium, a lower value, $2.8 \times 10^{-7}$, was obtained. At a [CDC$^-$] of 1 mM a large amount of precipitate formed. This happened even when no Cs was present in solution. Apparently, the solubility of NaCDC decreases in the highly concentrated salt solutions. If it is assumed that only NaCDC precipitates, then the $K_{sp}$ of NaCDC is about $1 \times 10^{-3}$. Using this value, the solubility of NaCDC in the medium can be calculated to be about 0.03 M.

Room temperature precipitation of CsCDC in the nitrate medium could not be carried out since NaCDC precipitated when small amounts of a highly concentrated NaCDC solution in water were added; however, this was not the case at 40°C. An experiment was carried out in which 5.1 mL of a 0.2 M NaCDC solution was added to a 25 mL solution of 10 mM CsNO$_3$, which was being stirred at 40°C. After stirring for 30 min, the solution was filtered, the precipitate washed with a small amount of water and the [CDC$^-$] determined in the filtrate was 0.6 mM. The precipitate was dried in air at 110°C and weighed (36.6 ± 0.5 mg - avg. of three experiments). A portion of the precipitated product was redissolved in water and the $[Cs^+]$ and [CDC$^-$] were measured. The
precipitate was 29.1% Cs and 71.6% CDC\(^-\). Pure CsCDC is 29.1% Cs, and 70.9% CDC. Ion chromatography showed that the precipitate had no Na or K present. Therefore, NaCDC precipitation does not occur at 40\(^\circ\)C in the nitrate medium when up to four equivalents of NaCDC solution is used; the precipitate contains only CsCDC. The value of \((K_{sp})^{ab}\) for the three experiments was \((3.9 \pm 0.5) \times 10^{-6}\), while the value for \((K_{sp})^{ma}\) was \((1.4 \pm 0.1) \times 10^{-6}\). Mass balance was achieved with CDC\(^-\) in the filtrate, precipitate and wash solutions.

**Solubility**

Precipitation experiments showed that the solubility of CsCDC was not the same in water, the nitrate medium and chloride medium. Because of these differences in CsCDC solubility, saturated CsCDC solutions were prepared at 30\(^\circ\)C with either NaCl or NaNO\(_3\) present. The [CDC\(^-\)] was measured by UV-visible spectroscopy, using a range of salt concentrations (0 to 4M NaCl and 0 to 5M NaNO\(_3\)). In Fig. 2, the logarithm of the CsCDC solubilities is plotted versus the square root of the ionic strength of the solutions. At low salt concentrations (< 0.1M), the Debye-Huckel limiting law is followed. There is some scatter in the data points due primarily to the low precision of the absorbance measurements. The solubility of CsCDC in 4M NaCl is about a third less than it is in water, while in 5M NaNO\(_3\) the solubility is slightly greater than in water.

The behavior of the CsCDC solubility with changes in the ionic strength is not very different from what might be expected with smaller, more hydrophilic anions. In Fig. 2 the solubility increases as the ionic strength increases, but then reaches a maximum value and begins to decrease. The two salt curves show basically the same behavior. But, the nitrate curve has a smaller curvature than that of the chloride curve.

The shape of the curves is similar to those found when the logarithm of the solubility of BaSO\(_4\) is plotted versus the ionic strength for a variety of salts.\(^{13}\) Even though BaSO\(_4\) is a +2/-2 1:1 salt, it has about the same solubility behavior as CsCDC. Unfortunately, no nitrates were used to provide the ionic strength in the BaSO\(_4\) study, just several chlorides (NaCl, KCl, CaCl\(_2\), and MgCl\(_2\)) , a bromide (KBr) and a borate (Na\(_2\)B\(_4\)O\(_7\)). All of the univalent cation and anion pairs showed about the same effect in changing the solubility of the BaSO\(_4\).
Hydroxide Reactivity

Since the formation of the CDC' anion is carried out in strong base solution, it was felt that it should have considerable base stability. The carborane ligand is formed by reacting 1,2-carborane with methanolic KOH at 40°:

\[
1,2-\text{B}_{10}\text{C}_{2}\text{H}_{12} + 2\text{OH}^- + 2\text{H}_2\text{O} \rightarrow [7,8-\text{B}_9\text{C}_2\text{H}_{12}]^- + \text{H}_2 + \text{B(OH)}_4^-
\]

The ions are then reacted with CoCl₂ in concentrated base to form CDC' :

\[
[7,8-\text{B}_9\text{C}_2\text{H}_{12}]^- + \text{OH}^- \rightarrow [7,8-\text{B}_9\text{C}_2\text{H}_{11}]^- + \text{H}_2\text{O}
\]

\[
[7,8-\text{B}_9\text{C}_2\text{H}_{11}]^- + 1.5 \text{CoCl}_2 \rightarrow [\text{Co((3)-1,2-C}_2\text{B}_9\text{H}_{11})_2]^- + 0.5\text{Co}^0 + 3\text{Cl}^-
\]

Reports have shown that neutral carboranes react with basic solutions. Wiesenbock and Hawthorne₁⁵ studied the reaction of the carborane in 50% EtOH - H₂O at 75° and established the following rate expression for the decomposition:

\[
\text{Rate} = 1.48 \times 10^{-3} \text{mol}^{-1}\text{s}^{-1}[1,2-\text{B}_{10}\text{C}_2\text{H}_{12}][\text{EtO}^-]
\]

If the [EtO⁻] is 1 M then the half-life would be 1.5 h. The 1, 7⁻¹⁶ and 1, 12⁻¹⁷ carboranes react more slowly with base since very rigorous conditions are required to remove one B atom from each cluster.

When CsCDC or NaCDC is dissolved in base solution, the solution may be yellow, orange to dark brown, depending on [CDC⁻]. As the reaction takes place, the solution slowly becomes colorless and a black solid appears. In all experiments with [CDC⁻] of 10⁻⁵ M at temperatures less than 65°C, trace amounts of a white precipitate were observed after about 20% of the CDC⁻ had reacted. The white precipitate appeared before the black precipitate was observed. In attempting to form more of the white precipitate, 0.5 mmol of CsCDC was placed in 50 mL of 3M NaOH and heated to 100°C for 13 h. The CsCDC completely dissolved, but no white precipitate was observed, only black precipitate and a dark brown solution.

Some of the reaction products have been identified. The black precipitate was isolated from one of the reactions, washed with water and dried. A sample of the black powder had an X-ray powder diffraction pattern that matched that of Co(O)OH. The ¹¹B nmr spectra showed that B(OH)₄⁻ is the final product for all of the boron. The intermediate
white precipitate was probably CsB₉C₂H₁₂ which has the protonated ligand of CDC⁻. However, it was not specifically identified; not enough could be recovered to be analyzed. One experiment which was carried out with 1M NaOH at 65°C and monitored by ion chromatography, showed that over a seven day period the [Cs⁺] decreased from 0.92 mM to 0.25 mM.

In examining H₂ as a product, the small pressure increase (10-20 torr, measured for the three similar experiments) was assumed to be due exclusively to H₂ production. These amounts were produced over long periods of time, which might have led to the lack of precision in the amount of H₂ measured. However, leaks in the container did not seem to be a problem since the pressure was always much less than atmospheric pressure and tests without H₂ showed no leaking. The mole ratio of H₂ to CDC⁻ decomposed for all of the experiments was less than one. With B(OH)₄⁻ as the end product of B, a much larger value was expected. The reason for the small amount of H₂ produced is not known.

The two UV-visible absorption bands of CDC⁻ (281 and 445 nm) may be used to follow the loss of CDC⁻ during the reaction. For dilute solutions with no nitrate present, the more sensitive 281 nm band may be used. With nitrate present, the 445 nm band was used to follow the reaction. As the reaction went to completion no new band appeared, until after about nine half-lives, a weak band at 360 nm began to form. Attempts were made to use procedures that took into account a change in the spectral baseline with time, but the data were not affected by these corrections. When the reaction was carried out at 75°C, the 360 nm peak appeared much earlier in the course of the reaction.

All of the reactions were carried out with an excess of OH⁻ present and the decrease in [CDC⁻] followed. The decrease obeyed first order kinetics and the rate constants (k) and half-lives for CDC⁻ decomposition at essentially constant [OH⁻] are given in Table 2. The temperature, [OH⁻], [NO₃⁻] and CDC⁻ counterion were varied. From a plot of ln(k) vs. 1/T (K) the following Arrehnius expression was found:

\[ \ln (k) = 34.4 - 1.33 \times 10^4 (1/T) \]

leading to an activation energy of 110 kJ/mol CDC⁻.

A fractional order of 1.26 for OH⁻ was obtained from the slope of the graph obtained by plotting ln k (at 65°C) vs. ln[OH⁻]. Therefore, with the large excess of OH⁻, the rate law is

\[ \text{Rate} = k_0 [\text{CDC}^-][\text{OH}^-]^{1.26} = k [\text{CDC}^-] \]
Varying [NO₃⁻] from 0 to 5M and using Na⁺ instead of Cs⁺ showed no major effect on the value of k. Using the rate and activation energy equations, the half-life of CDC⁻ at 25º in 1M OH⁻ was estimated to be 2.2 years.

Fig. 3 shows first-order plots for the 56º decomposition of 22 µM CsCDC and 14 mM NaCDC in 1M OH⁻. The former was determined using UV-visible spectroscopy, while the latter was determined with NMR. The rates are close, but the higher concentration of CDC⁻ shows a slightly smaller k value.

Since the reported solubility of the hexabromo compound, CsBCDC, in water is 3 x 10⁻⁴ M⁸, which is lower than that of CsCDC, a small amount of CsBCDC was prepared⁹ and the decomposition reaction carried out at 65º in 1 M NaOH. A 67 µM CsBCDC solution had a k value of 1.1 x 10⁻⁴ s⁻¹ or a 1.75 h half-life. For a similar solution of CsCDC the value of k is 20 x 10⁻⁷ s⁻¹ or a 98 h half-life. Substitution of three Br atoms for three H atoms on each of the two cages produces about a fifty fold increase in the rate of base decomposition. These results are expected if the reaction occurs by the nucleophilic attack of the hydroxide ion on one of the boron hydride cages.

Even though CDC⁻ is an inert d⁶ Co(III) π-complex, it still lacks great stability in the basic medium. The Co(III) is converted to the oxohydroxide and the ligands attached to the metal slowly undergo decomposition. This lack of stability at high [OH⁻] probably will mean that the CDC⁻ anion will not be able to serve as a precipitating agent for Cs⁺ at high pH.

Conclusions

Unfortunately, CsCDC does not have a low enough solubility or a high enough stability in aqueous base in order for NaCDC to be considered as a precipitating agent for Cs from base solution. If CsCDC was either a factor of ten less soluble in base or had a hydroxide decomposition rate constant about a hundred times smaller, the CDC⁻ might be a satisfactory anion to use for the precipitation. It might not be necessary to have both factors operating, since a very low solubility would not provide enough dissolved precipitate for reaction. Precipitation of ¹³⁷Cs using a precipitating agent, which forms a Cs salt with a higher solubility than that of CsTPB and low reactivity, might be achieved by adding non-radioactive ¹³³Cs to the waste and carrying out the process in stages. Efforts are underway to find a new Cs precipitating agent.
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REFERENCES


Table 1 Results of Precipitation of Cs+ with CDC- Solutions in Water and Cl Medium

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<th>(Ksp)\text{ab}</th>
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<td>Cl Med.</td>
<td>CDC- 46</td>
<td>1 x 10^{-3}***</td>
<td>1.5 x 10^{-3}</td>
<td>-</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

* - Symbols - PA, precipitating agent; (Ksp)\text{in}, Ksp from reagent concentrations at point of incipient precipitation; (Ksp)\text{ab}, Ksp from CDC absorbance value; (Ksp)\text{ac}, Ksp from direct [Cs] and [CDC-] measurements; Cl Med - 5M NaCl/0.1 M KOH/1.0M NaOH; TPB-, tetraphenylborate anion; CDC-, cobalt dicarbollide anion.

** - Assuming only NaCDC precipitates.

*** - Number of experiments carried out under these conditions.
Table 2. Results of OH$^-$ Reaction with MCDC.

<table>
<thead>
<tr>
<th>M</th>
<th>T(°C)</th>
<th>[OH$^-$] (M)</th>
<th>[NO$_3^-$] (M)</th>
<th>Initial [CDC$^-$] (μM)</th>
<th>k (s$^{-1}$)</th>
<th>$t_{1/2}$ (days)</th>
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</thead>
<tbody>
<tr>
<td>Cs</td>
<td>40</td>
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<td>0.97 x 10$^{-7}$</td>
<td>83</td>
</tr>
<tr>
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<td>0</td>
<td>22</td>
<td>8.8</td>
<td>9.2</td>
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<tr>
<td>Na</td>
<td>56</td>
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<td>0</td>
<td>14mM**</td>
<td>7.2</td>
<td>11.1</td>
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<tr>
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<td>0</td>
<td>35</td>
<td>20</td>
<td>4.1</td>
</tr>
<tr>
<td>Cs</td>
<td>65</td>
<td>1.0</td>
<td>0</td>
<td>1.5 mM**</td>
<td>19</td>
<td>4.3</td>
</tr>
<tr>
<td>Na</td>
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<td>0</td>
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<td>17</td>
<td>4.7</td>
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<tr>
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<td>0</td>
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<td>11</td>
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<td>19</td>
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<tr>
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<td>3.0</td>
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<td>19</td>
<td>4.3</td>
</tr>
<tr>
<td>Cs</td>
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<td>5.0</td>
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<td>4.4</td>
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</tr>
</tbody>
</table>

* - k obtained by following formation of [B(OH)$_4$]$^-$ using $^{11}$B nmr spectroscopy; other k values obtained by following loss of CDC$^-$ with UV-visible spectroscopy.

** - All other concentration values are μM.
FIGURE CAPTIONS

Fig. 1. Percent transmittance of a 10 mM solution of CsNO₃ measured at 600 nm as 0.1 mL amounts of a 75 mM solution of NaCDC(+) or NaTPB(Δ) were added.

Fig. 2. The logarithm of the solubility of CsCDC at 30°C in solutions of NaCl(+) and NaNO₃(Δ) plotted against the square root of the ionic strength.

Fig. 3. The first-order plots of the decomposition of CDC⁻ with 22 µM CsCDC (O) and 14 mM NaCDC(+) in 1 M OH⁻ at 56°C.