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CAESIUM COBALT DICARBOLLIDE—SOLUBILITY, PRECIPITATION AND REACTIVITY IN BASIC AQUEOUS SOLUTION

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Abstract—The title compound, $Cs^+[Co((3)\text{-}1,2\text{-}C_2B_9H_{11})_2]^-$ (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. $[Cs^+]$ and $[CDC^-]$ at the point of precipitation were estimated and approximate values of K_{sp} for CsCDC were determined at room temperature: 8×10^{-6} (water), 7×10^{-6} (1 M NaOH) and 2×10^{-6} (5M 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 10 mM Cs^+ solution at 40°C and the $[CDC^-]$ measured spectrophotometrically. Only CsCDC precipitated, and a K_{sp} of 3.9×10^{-6} was determined. The solubilities of CsCDC were measured in $NaNO_3$ and NaCl solutions at 30°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 μM CsCDC with NaOH (1 M) has a first-order rate constant at 56°C of 8.8×10^{-7} s^{-1}, while that for NaCDC (14 mM) is 7.2×10^{-7} s^{-1}. The activation energy for the reaction is 110 kJ mol^{-1}.

The removal of radioactive $^{137}Cs^+$ ions from nuclear waste solution is a major environmental problem. The removal may be achieved by ion exchange, extraction or precipitation.[1] 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 litres 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.[2,3]

A possible Cs^+ precipitating agent is $[Co((3)\text{-}1,2\text{-}C_2B_9H_{11})_2]^-$ (CDC^-), which was first prepared as the Cs^+ salt by Hawthorne and Andrews.[4] This

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boron cluster species with a π-bonded Co^{III} ion has recently been pointed out to have many potential uses.[5] It has been utilized on a large scale to extract Cs^+ from acidic aqueous solution into nitrobenzene.[6] CsCDC has a solubility in water of 0.975 mM at 23°C,[7] while CsTPB has a solubility of 0.028 mM at 20°C.[8] 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 *ca* 14) and concentrated in $NaNO_3$ (*ca* 5 M), 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",[9] 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 purchased 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(ε 35,000) and 445 nm (ε 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), $Cs^+Co(C_2B_9H_8Br_3)_2^-$, was prepared by the procedure of Hawthorne *et al.*[10] with a yield of 84% using CsCDC instead of RbCDC in the bromination reaction. The compound showed a UV band at 295 nm (13 000 M^{-1} cm^{-1}). ^{11}B NMR (acetone): δ 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–vis spectra.

(b) ^{11}B NMR spectra were obtained at 115.85 MHz with a Nicolet NT-360 spectrometer, which was externally referenced to $BF_3 \cdot OEt_2$. 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 cm^3 was injected into the instrument which was fitted with a 50 cm^3 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 1 cm^3 min^{-1} was used with suppressed conductivity being the detection mode. These are the approximate elution times (min): Na^+, 2; K^+, 3; Cs^+, 4. In order to detect 1 mM Cs^+ or less, $[Na^+]$ 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 *ca* 0.01 mM.

(d) A Gow-Mac 580 gas chromatograph (gc) with a Supelco 60/80 molecular sieve 5 Å column (3 ft × 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°C; He flow rate, 60 cm^3 min^{-1}; attenuation, 1X; and detector current, 250 mA.

(e) The X-ray powder diffraction pattern of the black product obtained from the reaction of CDC^- with base was determined by Dr William Pennington at Clemson University using a Scintag X-ray powder diffractometer. The pattern had only the lines of Co(O)OH.

Typical precipitation experiment

A solution (25 cm^3) of 10 mM CsCl was prepared using water or a given medium as solvent and 2 cm^3 were removed for the spectrophotometer reference. The precipitating agent (0.075 M NaCDC) was added in 0.1 cm^3 increments to the stirring solution. After each increment was added, the solution was allowed to stir for 5 min before the %T of a 2 cm^3 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 1 equiv. of precipitating agent (3.1 cm^3) was added. When complete, the flask was sealed, and the solution allowed to stir for more than 24 h. 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–vis spectrum of the solution and, if possible, $[Cs^+]$ 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–vis spectrum of the filtered solution obtained. [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 cm^3 of the desired [CDC^-] and [OH^-]. In some cases, solid $NaNO_3$ was added to produce a given [NO_3^-]. 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–vis spectrum was taken of each. The absorbance (A) was measured at 281 nm, or if NO_3^- 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* 14 mM) was prepared with 1.0 M NaOH and the ^{11}B 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.

H_2 *as a product*

The reaction was carried out three times on a vacuum line in order to detect and determine the amount of H_2 generated. The experiments used a 88.2 cm^3 vessel containing 0.20 g of CsCDC and 25 cm^3 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 H_2, O_2 and N_2. Due to the small amount of H_2 produced, the gc could qualitatively detect the presence of H_2, but not give the amount produced. The moles of H_2 were calculated from the small pressure increase, assuming only H_2 was formed. The change in the [CDC^-] may be made by measuring the UV–vis spectra or by using the rate equation. The moles of H_2 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.[11] 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 CsCl (10 mM) with NaCDC (0.075 M) and NaTPB (0.075 M) 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 K_{sp} for CsCDC may be obtained from the precipitation reaction in several ways. The

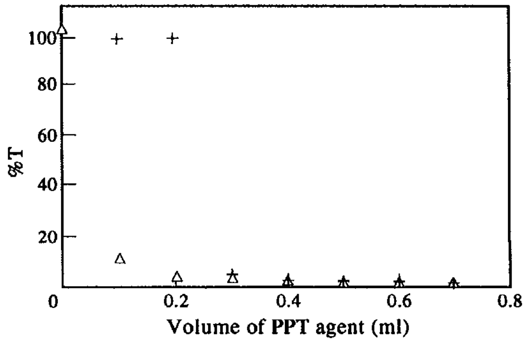

Fig. 1. Per cent transmittance of a 10 mM solution of $CsNO_3$ measured at 600 nm as 0.1 cm^3 amounts of a 75 mM solution of NaCDC(+) or NaTPB(Δ) were added.

incipient K_{sp}, $(K_{sp})^{in}$, is found from the turbidity curve (Fig. 1) by estimating [Cs^+] and [CDC^-] at the point of incipient precipitation. The absorbance K_{sp}, $(K_{sp})^{ab}$, is found when some CDC^- is added and the absorbance of the CDC^- remaining in solution is measured. [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 [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.[12] 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.[13]

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 [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 (5 M NaCl/0.1 M KOH/1.0 M NaOH). A nitrate medium (5 M $NaNO_3$/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 UV region, 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 at room temperature, the precipitation gave a K_{sp} of $(8 \pm 2) \times 10^{-6}$ for CsCDC. With Cs^+ (10 mM) in the chloride medium, a lower value, 2×10^{-6}, 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 1×10^{-3}. Using this value, the solubility of NaCDC in the medium can be calculated to be approximately 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 cm^3 of a NaCDC (0.2 M) solution was added to a solution (25 cm^3) of $CsNO_3$ (10 mM), 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—average of three experiments). A portion of the precipitated product was redissolved in water and [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 in the precipitate no Na or K were present. Therefore, NaCDC precipitation does not occur at 40°C in the nitrate medium when up to 4 equiv. 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. Due to these differences in CsCDC solubility, saturated CsCDC solutions were prepared at 30°C with either NaCl or $NaNO_3$ present. The [CDC^-] was measured by UV–vis spectroscopy, using a range of salt concentrations (0–4 M NaCl and 0–5 M $NaNO_3$). In Fig. 2, the logarithm of the CsCDC solubilities is plotted vs the square root of the ionic strength of the solutions. At low salt concentrations (<0.1 M), 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 NaCl (4 M) is about a third less than it is in water, while in $NaNO_3$ (5 M) the solubility is slightly greater than in water.

The behaviour 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 behaviour. However, 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 vs the ionic strength for a variety of salts.[14] Even though $BaSO_4$ is a $+2/-2$ 1 : 1 salt, it has a similar solubility behaviour to CsCDC. Unfor-

Table 1. Results of precipitation of Cs^+ with CDC^- solutions in water and Cl medium at room temperature

$[Cs^+]$ (mM)	Solvent	PA[a]	[PA] (mM)	$(K_{sp})^{in}$	$(K_{sp})^{ab}$	$(K_{sp})^{ac}$	[b]
10	Water	TPB^-	75	$<1\times10^{-7}$	—	—	1
10	Water	CDC^-	75	8×10^{-6}	—	—	1
10	Water	CDC^-	52	6×10^{-6}	4.5×10^{-6}	3.6×10^{-6}	2
5	Water	CDC^-	52	1×10^{-5}	4.5×10^{-6}	—	1
1	Water	CDC^-	52	8×10^{-6}	—	—	1
10	1M NaOH	CDC^-	52	7×10^{-6}	1.8×10^{-6}	—	1
10	Cl med	CDC^-	52	2×10^{-6}	2.7×10^{-7}	2.9×10^{-7}	2
1	Cl med	CDC^-	46	1×10^{-3}[c]	1.4×10^{-3}	—	9
0	Cl med	CDC^-	46	1×10^{-3}[c]	1.5×10^{-3}	—	2

[a] Symbols: PA, precipitating agent; $(K_{sp})^{in}$, K_{sp} from reagent concentrations at point of incipient precipitation; $(K_{sp})^{ab}$, K_{sp} from CDC absorbance value; $(K_{sp})^{ac}$, K_{sp} from direct [Cs] and $[CDC^-]$ measurements; Cl med-5 M NaCl/0.1 M KOH/1.0 M NaOH; TPB^-, tetraphenylborate anion; CDC^-, cobalt dicarbollide anion.

[b] Number of experiments carried out under these conditions.

[c] Assuming only NaCDC precipitates.

tunately, 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 ($Na_2B_4O_7$). All the univalent cation and anion pairs showed 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°C:[15]

$$1,2\text{-}B_{10}C_2H_{12}+2OH^-+2H_2O \rightarrow [7,8\text{-}B_9C_2H_{12}^-]+H_2+B(OH)_4^-.$$

The ions are then reacted with $CoCl_2$ in concentrated base[4,10] to form CDC^-:

$$[7,8\text{-}B_9C_2H_{12}^-]+OH^- \rightarrow [7,8\text{-}B_9C_2H_{11}^{2-}]+H_2O$$

$$[7,8\text{-}B_9C_2H_{11}^{2-}]+1.5CoCl_2 \rightarrow [Co((3)\text{-}1,2\text{-}C_2B_9H_{11})_2]^-+0.5Co^0+3Cl^-.$$

Reports have shown that neutral carboranes react with basic solutions. Wiesboek and Hawthorne[16] studied the reaction of the carborane in 50% $EtOH\text{-}H_2O$ at 75°C and established the following rate expression for the decomposition:

$$\text{Rate} = 1.48\times10^{-3}\,l\,mol^{-1}s^{-1}\,[1,2\text{-}B_{10}C_2H_{12}][EtO^-].$$

If $[EtO^-]$ is 1 M then the half-life would be 1.5 h. The 1, 7-[17] and 1, 12-carboranes[18] 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 colourless 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

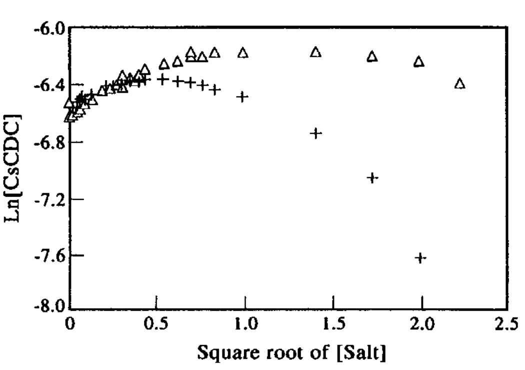

Fig. 2. The logarithm of the solubility of CsCDC at 30°C in solutions of NaCl(+) and $NaNO_3$(Δ) plotted against the square root of the ionic strength.

after 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, CsCDC (0.5 mmol) was placed in NaOH (3 M, 50 cm^3) and heated to 100°C for 13 h. The CsCDC completely dissolved, but no white precipitate was observed, only a 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 showed an X-ray powder diffraction pattern that matched that of Co(O)OH. The ^{11}B NMR spectra showed that $B(OH)_4^-$ is the final product for all the boron. The intermediate white precipitate might be $CsB_9C_2H_{12}$, which has the protonated ligand of CDC$^-$ and is reported to be insoluble in water.[15] However, it was not specifically identified; not enough could be recovered to be analysed. One experiment which was carried out with NaOH (1 M) at 65°C and monitored by ion chromatography, showed that over a 7-day period [Cs$^+$] decreased from 0.92 to 0.25 mM.

In examining H_2 as a product, the small pressure increase (10–20 torr, measured for the three similar experiments) was assumed to be due exclusively to H_2 production. These amounts were produced over long periods of time, which might have led to the lack of precision in the amount of H_2 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 H_2 showed no leaking. The mole ratio of H_2 to CDC$^-$ decomposed for all 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 H_2 produced is not known.

The two UV–vis 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 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,[19] 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 excess OH$^-$ present and a 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$^-$], [NO$_3^-$] and CDC$^-$ counter-ion were varied. From a plot of ln (k) vs $1/T$ (K) the following Arrhenius expression was found:

$$\ln(k) = 34.4\text{–}1.33 \times 10^4 (1/T),$$

leading to an activation energy of 110 kJ mol^{-1} CDC$^-$.

Table 2. Results of OH$^-$ reaction with MCDC

M	T (°C)	[OH$^-$] (M)	[NO$_3^-$] (M)	Initial [CDC$^-$] (μM)	k (s^{-1})	$t_{1/2}$ (days)
Cs	40	1.0	0	19	0.97×10^{-7}	83
Cs	56	1.0	0	22	8.8	9.2
Na[a]	56	1.0	0	14 mM[b]	7.2	11.1
Cs	65	1.0	0	35	20	4.1
Cs	65	1.0	0	1.5 mM[b]	19	4.3
Na	65	1.0	0	19	17	4.7
Cs	65	0.5	0	36	11	7.5
Cs	65	2.0	0	41	60	1.3
Cs	65	3.0	0	33	96	0.8
Cs	65	1.0	1.0	15	19	4.4
Cs	65	1.0	3.0	18	19	4.3
Cs	65	1.0	5.0	16	18	4.4
Cs	65	0.32	5.0	16	4.4	18

[a] k obtained by following the formation of $[B(OH)_4]^-$ using ^{11}B NMR spectroscopy; other k values obtained by following the loss of CDC$^-$ with UV–vis spectroscopy.

[b] All other concentration values are μM.

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:

$$\text{rate} = k_0[\mathrm{CDC}^-][\mathrm{OH}^-]^{1.26} = k[\mathrm{CDC}^-].$$

Varying $[NO_3^-]$ from 0 to 5 M 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 25°C in OH^- (1 M) was estimated to be 2.2 years.

Fig. 3 shows first-order plots for the 56° decomposition of CsCDC (22 μM) and NaCDC (14 mm) in OH^- (1 M). The former was determined using UV–vis 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 3×10^{-4} M,[9] which is lower than that of CsCDC, a small amount of CsBCDC was prepared[10] and the decomposition reaction carried out at 65°C in NaOH (1 M). A 67 μM CsBCDC solution had a k value of 1.1×10^{-4} s^{-1} or a 1.75 h half-life. For a similar solution of CsCDC the value of k is 20×10^{-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 a 50 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 d^6 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.

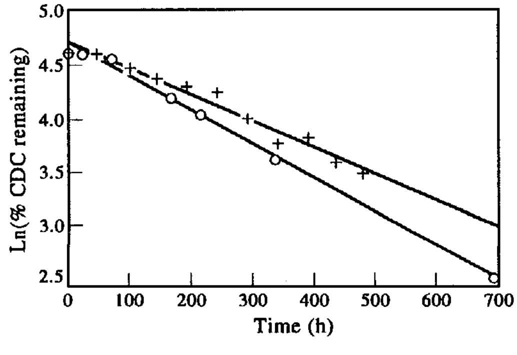

Fig. 3. The first-order plots of the decomposition of CDC^- with 22 μM CsCDC (O) and 14 mM NaCDC(+) in 1 M OH^- at 56°C.

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 10 less soluble in base or had a hydroxide decomposition rate constant 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 ^{137}Cs 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 ^{133}Cs to the waste and carrying out the process in stages. Efforts are underway to find a new Cs precipitating agent.

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