

Electron Transfer Reactions in Organic Chemistry. XI.* The Reaction between Carbon Tetrabromide and the Cage Complex [Co(II)sepulchrates]²⁺. A Kinetic and Product Study

Lennart Ebersson** and Mikael Ekström

Division of Organic Chemistry 3, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden

Ebersson, L. and Ekström, M., 1987. Electron Transfer Reactions in Organic Chemistry. XI. The Reaction between Carbon Tetrabromide and the Cage Complex [Co(II)sepulchrates]²⁺. A Kinetic and Product Study. – Acta Chem. Scand. B 41: 41–49.

A kinetic and product study of the reaction between CBr₄ and the cage complex [Co(II)sepulchrates]²⁺ in CH₃CN/H₂O at 20 °C has been performed. The reaction was found to be first order in both CBr₄ and [Co(II)sepulchrates]²⁺, the only products found being CHBr₃ and C₂Br₆. The mechanism is discussed and suggested to be an outer-sphere electron transfer mechanism, with a rate constant for the rate determining electron transfer step $k_{ET} = 0.020 \text{ M}^{-1} \text{ s}^{-1}$ (CH₃CN/H₂O [64/36 (v/v)]; [Tris] 36 mM, [HClO₄] 3.6 mM and [NaClO₄] 9.1 mM). The possibility that the complexation chemistry of CBr₄ might influence the reaction is critically considered.

Recently, much work has been published¹ concerning the possible electron transfer (hereafter denoted ET) nature of the reduction of the carbon–halogen bond by different reagents such as radical anions, carbanions and metal complexes. Three mechanisms are discussed in this context, namely oxidative addition (S_N or X-philic mechanism, metal complexes only), halogen atom transfer and ET.^{1m} Polyhalogenated aliphatic compounds are of particular interest since they are more easily reduced than the simple aliphatic monohalides,² the polarographic $E_{1/2}$ values becoming less cathodic in the order CH₃X < CH₂X₂ < CHX₃ < CX₄ for polyhalomethanes. A provisional E° value of ca. –0.25 V vs. NHE has been estimated for the reduction of carbon tetrachloride.^{1a} Moreover, there is evidence³ (ESR) that the radical anions of CX₄ (X = Cl, Br) have some stability in a solid matrix at 77 K, in contrast to the nonexistence of radical anions of monohalides.⁴ Finally, the weak ET oxidizing character of polyhalogen aliphatics might be connected

with the mechanism of their long-term toxicity⁵ (formation of reactive neutral radicals via reduction and carbon–halogen cleavage). We have therefore initiated a study of the possible outer-sphere ET reactions of polyhalogenated aliphatic compounds.

Reagents used for the reduction of polyhalogenalkanes include metal complexes,⁶ organic molecules,⁷ superoxide ion⁸ and the solvated electron.⁹ In line with our current interest in ET-mediated processes, we are trying to define conditions under which outer-sphere ET processes become feasible. One possibility is to use ET reagents which by their very structure are prohibited from undergoing polar reactions, as for example in the oxidation of 4-methoxytoluene with 12-tungstocobalt(III)ate ion,¹⁰ a cluster ion with the oxidizing center deeply buried inside a shell of tungsten oxide octahedra which expose only nonbasic oxygens toward the solution.¹¹

In this study, Co(II)sepulchrates, 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosanecobalt(II) [Fig. 1; hereafter denoted Co(II)sep], first prepared by Sargeson *et al.*¹² was chosen for a pilot study with carbon tetrabromide as the oxidant.

*Part X, see Ref. 29.

**To whom correspondence should be addressed.

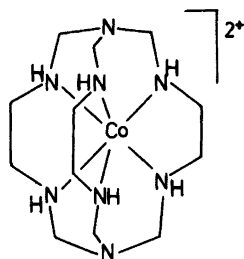


Fig. 1. The $[\text{Co(II)sepulchrato}]^{2+}$ ion.

This complex has the properties desired from an outer-sphere reagent: Co(II) is buried inside a cage of a single organic ligand, which in its turn exposes only nitrogens of very low basicity and nucleophilicity toward the solution. It consists of a central octahedrally coordinated cobalt ion with six bonding nitrogens derived from three 1,2-ethanediamine (en) units. The complex is further stabilized by bonding the three en ligands with the tripodal $\text{N}(\text{CH}_2-)_3$ unit on both sides (Fig. 1). The resulting cage complex is substitution-inert in both the Co(II) and Co(III) state and thus should be a good model for an outer-sphere ET reagent, as shown in studies of its reactions with inorganic metal complexes¹³ and nonmetallic inorganic species.^{14,15} Its $E^\circ[\text{Co(III)/Co(II)}]$ of -0.30 V vs. NHE*¹⁵ gives a suitable range of rate constants with carbon tetrabromide as the oxidant. The self-exchange rate constant for the Co(III)sep/Co(II)sep couple is known: $5.1 \text{ M}^{-1} \text{ s}^{-1}$ at 25°C in H_2O .¹⁵

Experimental

Special glassware. To be able to deaerate small volumes of reagent and substrate solutions in a convenient way, a special type of glass device, here called WB (after WickBerg), was used.¹⁶ The high-purity argon was transported in nylon (O.D. 3.2 mm) or teflon (O.D. 3.2 or 1.2 mm) tubes. These were inserted into the WB, which consisted of a piece of glass tubing with a constriction so as to assure a tight junction between the glass and the plastic tube, but at the same time allowing the plastic tubes to be further inserted or withdrawn (Fig. 2).

*Normal hydrogen electrode. All potentials referred to in this paper are given with this reference.

All vessels to be used in the oxygen-sensitive experiments were equipped with a pair of these devices, and a protruding short glass tube to which a rubber septum could be attached. Thus in the smallest vessel, with WB for 1.2 mm O.D. tubes, volumes down to 0.5 ml could conveniently be deaerated and stored without loss of solvent or substrate.

Chemicals. Co(III)sep was prepared according to the method given by Sargeson *et al.*¹⁵ The structure was confirmed by its NMR (Jeol MH 100) and UV spectra. CBr_4 was Fluka *purum* and was sublimed in vacuum at 70°C . CBrCl_3 was from Janssen (Gold label) and C_2Br_6 was a gift from Dr. A.-B. Hörnfeldt at this Department. The water was doubly quartz-distilled. D_2O was from Ciba-Geigy and of 99.8% isotopic purity. Baker HPLC quality CH_3CN was used without further purification. All other chemicals were of analytical quality and were used as received.

Preparation of the Co(II)sepulchrato solutions. Co(III)sep was electrochemically reduced in a three-compartment cell, fitted with Haldenvanger ceramic frits between the compartments. The reductions were run at constant potential by an Amel potentiostat equipped with a current integrator. An Hg pool was used as cathode and a Pt wire as anode. The reference electrode was a polished Ag wire in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ [60/40 (v/v)] 10 mM NaClO_4 solution connected to the catholyte through a porous pin.

A typical preparation was performed as follows: 10–20 ml of a 2 mM solution of Co(III)sep Cl_3 in the appropriate medium was placed in the cathode compartment, and the same solution

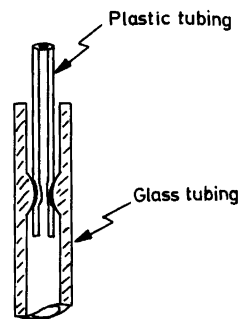


Fig. 2. The WB device.

without the Co(III)sepCl₃ in the two other compartments. The compartments and their contents were simultaneously deaerated by bubbling high purity Ar through the solutions with the aid of high porosity frits for about 30 min. The catholyte was then protected by passing a slow stream of high purity Ar through the catholyte compartment during the electrolysis. The potential was set at -0.6 to -0.7 V vs. the reference electrode, i.e. -(0.3-0.4) vs. NHE. About 1F/1 mol of Co(III)sep was passed through the cell at ambient temperature; the catholyte turned from brown-yellow to colourless.

The reduced solution could be transferred with gas-tight syringes, either directly for use in product or kinetic studies, or to a previously deaerated storage vessel. Here, it could be stored for at least two days protected by a very slow stream of high-purity Ar.

Product studies. A 5.0 mM solution of Co(II)sep (20 ml) in the appropriate medium (see Results) was transferred to a deaerated reaction vessel. To this was added 2.00 ml of a deaerated solution of 0.100 M CBr₄ in CH₃CN. The reaction was run at ambient temperature and protected by a very slow stream of Ar through the vessel. Reaction times were at least 3 h for basic and 2 h for acidic solutions. After completion of the reaction 10 ml of water were added and, if acidic, the reaction mixture was neutralized with saturated NaHCO₃ solution. The resulting mixture was extracted 3× with 5 ml of CH₂Cl₂, BrCCl₃ being added as internal standard with the first portion. The combined organic phases were washed once with water, dried with MgSO₄ and the MgSO₄ filtered off. The work-up was performed by stirring the two-phase system in a conical flask with a magnetic stirrer (thus avoiding too much evaporation of the highly volatile products and making it easier to protect the reaction mixture from incident light). Care was taken not to expose the mixture to light as the polybrominated halocarbons are sensitive to UV light. Due to the high volatility of the polyhalocarbons, 1 ml of the filtrate was saved for quantitative product studies by GLC. The rest was gently evaporated to ~1 ml, searched for trace products and used for GC/MS analysis. No other peaks, except those of CHBr₃ and C₂Br₆, were detected, the detection limit being ≤0.1%. The GC analysis was performed on a Varian 3300 chromatograph equipped with a

J&W DB-1 15 m megabore column and a FI detector. A Finnigan 4021 mass spectrometer run at 19 eV and equipped with a 10 m SE-30 capillary column was used for the GC/MS analysis. This was used only to analyze the product runs in CH₃CN/D₂O (see Results). The major peaks for the two products found were: CDBr₃ *m/e* (rel. int.) 257(4), 255(8), 253(10), 251(5), 176(44), 174(100), 172(51). C₂Br₆ *m/e* (rel. int.) 348(13), 346(61), 344(100), 342(67), 340(17), 267(7), 265(28), 263(29), 261(9), 186(4), 184(9), 182(4).

Kinetics. All kinetics were run at 20.0±0.1°C in the thermostatted cell compartment of a Cary 219 UV/Vis spectrophotometer, equipped with a digital interface port and connected to an HP-85 microcomputer. To a cuvette thoroughly deaerated with high purity Ar and sealed with a rubber septum, 2.50 ml of Co(II)sep solution was added with the help of a gas-tight syringe. The cuvette was placed in the spectrophotometer and allowed to equilibrate for a few min. A deaerated solution of CBr₄ in CH₃CN (0.250 ml), protected from light, was added with a gas-tight syringe. The reaction was followed at 474 nm, 200 data points being collected automatically at regular intervals and stored on magnetic tape. The data set was then analyzed on an HP-9835 tabletop computer by the non-linear regression method developed by Marquardt.¹⁷

Cyclic voltammetry. Cyclic voltammograms were recorded at ambient temperature with the CV equipment developed by Hammerich and Parker.¹⁸ An Hg/Pt electrode, to which the mercury had been adsorbed by electroreduction from a saturated HgCl₂ solution, was used as working electrode. The sepulchrate solution had to be deaerated before recording the voltammograms. No IR compensation was used.

The pH measurements were made with a Radiometer pH meter employing a combination glass electrode. In the H₂O/CH₃CN mixtures studied the electrode exhibited quick response and no drift.

Results

Product studies in slightly basic solution. A product study was carried out under conditions similar to those used in the buffered kinetic runs: tem-

perature $\sim 20^\circ\text{C}$; $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ [64/36 (v/v)]; $[\text{Co(II)sep}]$ 4.55 mM; $[\text{CBr}_4]$ 9 mM; $[\text{NaClO}_4]$ 8 mM; $[\text{HClO}_4]$ 9.1 mM; $[\text{Tris}]^*$ 91 mM. Only two products were found: CHBr_3 and C_2Br_6 .

Runs were also made where H_2O was exchanged for D_2O , and these gave the same product composition but with the bromoform 98% deuteriated. From these runs, the products were unambiguously identified through their mass spectrograms, which were compared to the mass spectrograms of authentic samples of CHBr_3 and C_2Br_6 . The $\text{CDBr}_3/\text{CHBr}_3$ ratio was also determined from the mass spectrograms by comparing the relative intensities for the four CDBr_3^+ peaks 257, 255, 253 and 251 *m/e*, with the four CHBr_3^+ peaks 256, 254, 252 and 250 *m/e*. Thus, the yield as determined from five runs, calculated on the basis of a consumption of 2 mols of Co(II)sep /mol per mol of CHBr_3 (see Discussion) and per mol of C_2Br_6 was: CHBr_3 , 84% and C_2Br_6 , 4%. Losses due to $<100\%$ current efficiency in the reduction to Co(II)sep or to possible O_2 reaction with Co(II)sep were not accounted for.

Product studies in acidic solution. The conditions were the same as for the slightly basic solutions, but no Tris was added. No additional products

*Tris = Tris(hydroxymethyl)aminomethane.

were found. The bromoform was 98% deuteriated when D_2O was used. The yields were: CHBr_3 , 70% and C_2Br_6 , 10%, as determined from five runs.

Kinetics, UV/Vis spectra and data treatment

General. All kinetics were run at $20.0 \pm 0.1^\circ\text{C}$ and followed by monitoring the appearance of Co(III)sep at 474 nm. All runs were performed under pseudo-first order conditions, the $[\text{CBr}_4]/[\text{Co(II)sep}]$ ratio normally being 33 but never less than 10. The observed rate constant was calculated by fitting the collected data to a two-parameter function [eqn. (1)], using the non-linear regression method developed by Marquardt.¹⁷

$$A = A_\infty + (A_0 - A_\infty)\exp(-k_{\text{obs}} t) \quad (1)$$

Eqn. 1 is the normal first-order expression, where A denotes absorbance. The two parameters were k_{obs} and A_∞ . The value for A_0 was taken directly from the experiments. The calculated A_∞ was checked to be in reasonable agreement ($\pm 10\%$) with the expected A_∞ calculated from Lambert-Beer's law. For each run, the whole collected data set, covering approximately 4 half-lives, was used in the calculations and no data were discarded if not explicitly stated.

Table 1. Dependence of k_{obs} on different concentration parameters; $[\text{CBr}_4]$ 60.1 mM; $[\text{Co(II)sep}]$ 1.8 mM.

Entry No.	$[\text{NaClO}_4]/$ mM	[Buffer]/ mM; mM	pH ^a in H_2O	pH ^a in 64% CH_3CN	$\text{CH}_3\text{CN}/$ vol. %	$k_{\text{obs}}/$ min^{-1}	$\text{SSR}/10^{-5}$ ^b
1	12.7	—			64	0.13	50
2	10.9	Tris 18, HClO_4 1.8	9.3		64	0.13	3
3	9.1	Tris 36; HClO_4 3.6	9.3	8.7	64	0.14	4
4	5.4	Tris 73; HClO_4 7.3	9.3		64	0.14	1
5	9.6	Tris 3.6; HClO_4 3.1	7.5	7.2	64	0.15	7
6	—	NaOAc 12.7; AcOH 7.1	5.0	5.4	64	0.26	100
7	—	NaOAc 12.7; AcOH 635	3.0	4.4	64	0.34	60
8	3.6	HClO_4 9.1	2.0	1.8	64	0.14 ^c	3 ^c
9	9.1	Tris 36; HClO_4 3.6	9.3		50	0.16	1
10	9.1	Tris 36; HClO_4 3.6	9.3		82	0.17	2
11	9.1 ^d	Tris 36; HCl 31	7.5		64	0.22	2
12	9.1	Tris 36; HClO_4 31	7.5		64	0.16	10
13	9.1 ^e	Tris 36; HClO_4 36	9.3		64	0.18	3

^aSee text. ^bSum of the squared residuals, see text. ^cCalculated from the exponential part of the curve, see text. ^d NaCl was used instead of NaClO_4 . ^e NaBr was used instead of NaClO_4 .

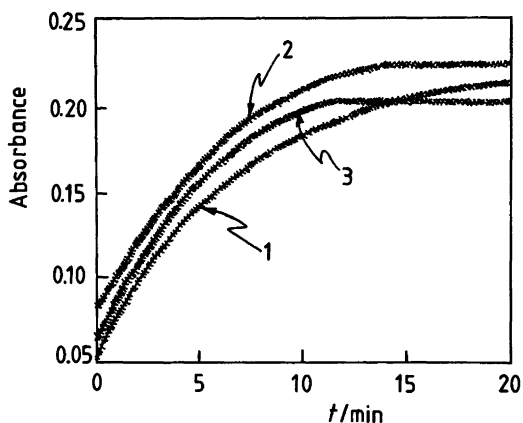


Fig. 3. Successive runs at pH 2 (see text). 1. About 0.5 h after the onset of the reduction of Co(III)sep. 2. Second run about 0.5 h later. 3. Third run about 1 h later. The curves have been slightly displaced in the vertical direction in order to be distinguishable.

The visible spectrum of Co(III)sepCl₃ in 64% CH₃CN, 36% H₂O, with and without buffers, was identical to the spectrum in pure water described by Sargeson *et al.*¹²

Unbuffered solutions. The reaction between CBr₄ and Co(II)sep produced ~1 mol OH⁻/2 mols of Co(II)sep (see Discussion). In unbuffered solutions, this was seen by the reaction mixture being red* after completion due to the deprotonation of one (or several) of the secondary amines in the cage. The pK_a of deprotonation of these amines has been estimated to be 13–14,¹⁵ a high value compared to those of organic amines¹⁹ but consistent with the pK_a of 14.9 for [Co(en)₃]³⁺.²⁰ The original colour was restored upon acidification.

The spectrum found after completion of the reaction could be reproduced exactly by adding the amount of OH⁻ (0.9 mM) required by the reaction stoichiometry to a Co(III)sep solution composed as the Co(II)sep solution in the unbuffered reaction. The deprotonation behaviour of the sepulchrate cage has already been described for water solutions,¹⁵ although at much higher [OH⁻] (about 0.1 M).

Despite this colour change, the kinetics were very good, being highly reproducible (±5%) and clearly conforming to pseudo first-order behav-

our. The observed rate constant in unbuffered solution was identical to the observed rate constant within experimental error in the Tris/HClO₄-buffered runs (Table 1).

Buffered solutions. In our search for a medium giving well-behaved kinetics for the reaction under study, it was clearly seen that the acidity of the medium was of importance, and this urged us to undertake a more detailed investigation. To be able to at least qualitatively compare different buffer systems, pH values for the systems were needed. Values from measurements with the glass electrode and values calculated from known pK_a's in water are given in Table 1. The differences between the values in CH₃CN/H₂O mixtures and in pure water are, at least qualitatively, the ones to be expected for AcOH/AcO⁻ buffers,²¹ strong acid solutions²¹ and amine bases.²² The glass electrode values could thus be justified as approximate measures of the relative acidities of the solutions. These values are referred to in the ensuing discussion.

A Tris/HClO₄ buffer was used to obtain pH 8.7 and pH 7.2 and an AcOH/NaOAc buffer to obtain pH 5.4 and pH 4.4. A 10 mM HClO₄ solution produced the pH 1.8 solutions. The ionic strength was kept constant at 0.023 M. The calculated k_{obs}, the SSR (sum of the squared residuals) and the concentrations used are listed in Table 1. The SSR measures the deviations of eqn. (1) from the experimental data. Here, a value of ≤10⁻⁴ can be regarded as indicating a very good fit, while higher values indicate deviations. At pH 8.7 and pH 7.2 the kinetics were excellent, giving perfect fits and good reproducibility; generally the variation of k_{obs} was ≤±5%. At acidic pH's the fits were somewhat worse and the reproducibility ±10%. This was clearly due to the ageing of the Co(II)sep solution. Thus at pH 5.4 and 4.4 the reaction between CBr₄ and Co(II)sep became faster with ageing of the Co(II)sep solution (less than 1 h between the runs). A freshly prepared solution of Co(II)sep at pH 1.8 (30 min old from the onset of the electrolysis) gave in the first run impeccable kinetics with a rate constant equal to the rate constant at pH 8.7. However, in the following runs (30 min between each run), the kinetics were less well behaved, the absorbance end value being obtained abruptly (Fig. 3). The rate constant calculated from the initial exponential part was, however, the same as in the

*The Co(III)sep complex is yellow in neutral solutions.

Table 2. Dependence of k_{obs} on $[\text{CBr}_4]$. The other parameters were: CH_3CN 64 %; $[\text{NaClO}_4]$ 9.1 mM; $[\text{Tris}]$ 36 mM; $[\text{HClO}_4]$ 3.6 mM; $[\text{Co(II)sep}]$ 1.8 mM.

No. of runs	$[\text{CBr}_4]/\text{mM}$	$k_{\text{obs}}/\text{min}^{-1}$
2	19.2	0.0493
2	28.8	0.0716
2	48.0	0.123
2	76.7	0.180
2	115	0.258

first run. These deviations could be explained by the known fact that the Co(II)sep cage is unstable in acid,¹⁵ probably being degraded by initial protonation of the cage nitrogens.

Complexation chemistry of CBr_4 . Since it is known that CBr_4 forms complexes with many amines in aprotic solvents,²³ the effect of varying the amine concentration while keeping the $[\text{ClO}_4^-]$ and pH constant was determined (Table 1, entries 2–4). It is evident that the buffer system $\text{Tris}/\text{HClO}_4$ did not affect k_{obs} at the concentrations used. Also, no charge transfer bands could be found in the UV spectrum of a mixture of CBr_4 and Tris . This was also true for mixtures of Co(III)sep with CBr_4 , where complexation between CBr_4 and the secondary or tertiary nitrogens in principle should be feasible. An effort to produce the putative complex by evaporation of a solution of CBr_4 and Co(III)sep in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ also failed, as judged from an ESCA* spectrum of the nitrogens in the cage.²⁴ The ESCA spectra were identical for Co(III)sep alone and for the $\text{CBr}_4/\text{Co(III)sep}$ mixtures.

The complexation chemistry of CBr_4 also involves halide ions.²⁵ The presence of Cl^- from Co(III)sepCl_3 and of Br^- formed during the reaction [eqns. (3)–(7)] urged us to perform control experiments to check their influence on the reaction. The results for Cl^- (Table 1, entries 11 and 12) and for Br^- (entries 3 and 13) showed only a slight increase in reaction rate.

Solvent composition. Only a slight variation in the solvent composition was possible as CBr_4 is insoluble in water and Co(III)sepCl_3 is insoluble in CH_3CN . Thus runs were made with 82, 64, and

50 % CH_3CN (Table 1, entries 10, 3 and 9) corresponding to dielectric constants³ 43.7, 51.8 and 58.4. As can be seen in Table 1, no trend was observed and the differences in k_{obs} were too small (almost within experimental error) to be attributed to any solvent effect.

Reaction order. The reaction order in CBr_4 was determined by varying the concentration of CBr_4 and plotting $\log k_{\text{obs}}$ vs. $\log[\text{CBr}_4]_0$ (Table 2 and Fig. 4). The other concentrations were kept constant at: CH_3CN 64 %; $[\text{NaClO}_4]$ 9.1 mM; $[\text{Tris}]$ 36 mM; $[\text{HClO}_4]$ 3.6 mM. The plot gave a slope of 0.93 in reasonable agreement with the expected slope of 1.0 for a second-order reaction. The second-order rate constant calculated from these runs and eqn. (7) (see Discussion) is $k_{\text{ET}} = 0.020(2) \text{ M}^{-1} \text{ s}^{-1}$.

Cyclic voltammetry. The electrochemistry of Co(III)sepCl_3 was studied at $\sim 20^\circ\text{C}$ in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ [64/36 (v/v)], 0.1 M NaClO_4 at pH 3 ($[\text{Tris}]$ 40 mM; $[\text{HClO}_4]$ 4 mM), at pH 7 (no buffer) and at pH 2 ($[\text{HClO}_4]$ 10 mM). The behaviour was essentially the same as found in water,⁹ i.e. all three solutions gave a quasi-reversible wave with a peak separation of 80–160 mV (the larger separation for the acidic solution) and an E° value of -0.30 V vs. NHE, calculated as the arithmetic mean between the anodic and cathodic peak potentials.

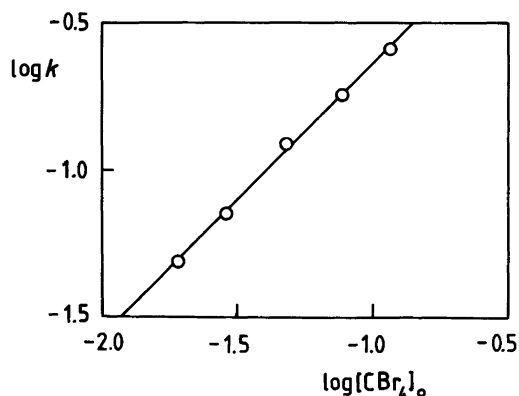


Fig. 4. Plot of $\log k_{\text{obs}}$ vs. $\log([\text{CBr}_4]_0/\text{M})$.

*From linear interpolations of data taken from the literature.²⁶

*Electron Spectroscopy for Chemical Analysis.

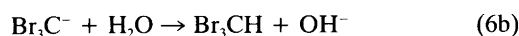
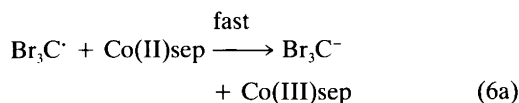
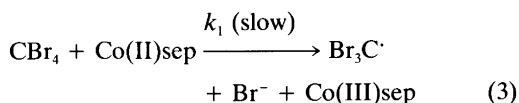
Discussion

The well-behaved pseudo first-order kinetics found in neutral and slightly basic medium, and the slope of 0.9 for the plot of $\log k_{\text{obs}}$ vs. $\log[\text{CBr}_4]_0$, gave a rate law according to eqn. (2).

$$\frac{d[\text{Co(III)sep}]}{dt} = k_{\text{obs}} [\text{CBr}_4] [\text{Co(II)sep}] \quad (2)$$

The formation of C_2Br_6 is good evidence for the intermediacy of $\text{Br}_3\text{C}^\cdot$ in the reaction. Furthermore, the low yield of C_2Br_6 and the almost exclusive formation of CDBr_3 in preference to CHBr_3 in the runs performed in $\text{CH}_3\text{CN}/\text{D}_2\text{O}$, show that almost all tribromomethyl radical is further reduced to the tribromomethanide anion. This is also in accord with the formation of 0.5 mol of $\text{OH}^-/1$ mol of Co(II)sep , clearly seen when the reaction is run in unbuffered medium.

Returning to the three principal mechanisms for reduction of alkyl halides by transition metal complexes mentioned in the introduction, only the ET mechanism seems to be in agreement with the experimental facts. Oxidative addition can hardly be a plausible alternative. It would require both the formation of a Co(IV) complex and the disruption of the sepulchrate cage, and cannot explain the products formed. Likewise, halogen atom transfer to the cobalt ion can be excluded on the basis that all Co(III)sep was recovered after the reaction, thereby proving that the cage had not been destroyed. All facts presented so far point towards the mechanism of eqns. (3)–(6).



Radicals are reduced very rapidly, so it is reasonable to apply the steady-state assumption to $[\text{Br}_3\text{C}^\cdot]$. Neglecting the reactions of eqns. (4) and (5), we get eqn. (7):

$$v = 2 k_1 [\text{CBr}_4][\text{Co(II)sep}] \quad (7)$$

However, another possibility that must be discussed is that CBr_4 can complex or react directly with the cage surrounding the cobalt ion. As already mentioned, polyhaloalkanes are known both to complex²³ and react²⁷ with amines. The sepulchrate cage, having two tertiary and six secondary nitrogens, should thus superficially be prone to interact with CBr_4 , but the lack of experimental evidence for any interaction between Co(III)sep and CBr_4 does not support this possibility.*

Moreover, Sargeson *et al.*¹⁵ advocate that the tertiary nitrogens in the cage are sp^2 -hybridized, with the remaining nonhybridized p_z orbital participating in bonding with the antibonding components of the $-\text{CH}_2-$ molecular orbitals of the cap. This is seen in, for example, the extremely low basicity of these nitrogens (pK_a of corresponding acids <0). Of course, the lack of a "free" lone pair on the nitrogens should also hamper the reaction or complexation with CBr_4 . The secondary nitrogens are bonded to the cobalt, thereby rendering any interaction with CBr_4 impossible.

The possibility that CBr_4 complexes with other molecules and ions present, i.e. Tris , Br^- and Cl^- must also be considered. From a kinetic point of view at least, this does not seem to be the case for Tris , as shown above. It must be noted that the complexation chemistry of polyhaloalkanes with amines²³ and halide ions²⁵ refers to aprotic solvents, and the interactions are very weak as deemed from the low complexation constants (1 M^{-1}). In the protic solvent used here, the hydrogen-bond-forming water will compete with CBr_4

*However, preliminary experiments show that the deprotonated form of the cage ion may act as a reducing agent. Thus, at a sufficiently high pH, Co(III)sep reduced the heteropoly ion $\text{Co(III)W}_{12}\text{O}_{40}^{5-}$ ($E^\circ = 1.0 \text{ V}$) as evidenced by the formation of the blue $\text{Co(II)W}_{12}\text{O}_{40}^{6-}$. This is further confirmed by cyclic voltammetry, which in addition to the quasi-reversible wave due to the $\text{Co(III)sep}/\text{Co(II)sep}$ couple, gives an irreversible peak at around $+0.15 \text{ V}$.

for the amines and halides, preventing the formation of the weak CBr_4 complexes. This explanation makes it unlikely that the small rate changes seen when exchanging ClO_4^- for Br^- or Cl^- are due to complexation between CBr_4 and the halide ion. Instead, differences in ion pairing between Co(II)sep and Cl^- , Br^- and ClO_4^- seem to be a likely explanation.²⁸ In this context, it is worth mentioning that the electron transfer reaction between ferrocene and *N*-bromosuccinimide has been shown²⁹ to be accelerated when *N*-bromosuccinimide is complexed to bromide ion. The ion pairing explanation is also in line with the results for solutions of different pH, where the only rate constants deviating from the normal value of $\sim 0.14 \text{ min}^{-1}$ are found when AcO^- has been used instead of ClO_4^- . Yet, both higher and lower pH had been used in the experiments with ClO_4^- .

Returning to the acidity of the solution, it is evident that the only effect of lowering the pH is to initiate the breakdown of Co(II)sep . The rate of the reaction between CBr_4 and Co(II)sep did not seem to be influenced. This argument is further strengthened by the fact that the electrochemical reduction of the C-Hal bond is known to be insensitive to changes in pH.^{2b} Furthermore, Co(II)sep is neither protonated nor deprotonated in the pH range used.¹⁵

Concluding, the results are best explained by an ET reaction between an uncomplexed CBr_4 and Co(II)sep , with the ET step rate-determining according to eqns. (3)–(7).

Acknowledgement. Financial support from the Swedish Natural Science Research Council is gratefully acknowledged.

References

- (a) Ebersson, L. *Acta Chem. Scand., Ser. B* 36 (1982) 533; (b) Ashby, E. C., Su, W.-Y. and Pham, T. N. *Organometallics* 4 (1985) 1499; (c) Ashby, E. C., De Priest, R. N., Goel, A. B., Wenderoth, B. and Pham, T. N. *J. Org. Chem.* 49 (1984) 3545; (d) Freeman, P. K. and Hutchinson, L. L. *J. Org. Chem.* 48 (1983) 4705; (e) Garst, J. F. *Acc. Chem. Res.* 4 (1971) 400; (f) Okabe, M. and Tada, M. *Bull. Chem. Soc. Jpn.* 55 (1982) 1498; (g) Lee, K.-W. and San Filippo, J., Jr. *Organometallics* 1 (1982) 1496; (h) Kochi, J. K. and Powers, J. W. *J. Am. Chem. Soc.* 92 (1970) 137; (i) Bakac, A. and Espenson, J. H. *J. Am. Chem. Soc.* 108 (1986) 713; (j) Andrieux, C. P., Gallardo, I., Savéant, J.-M. and Su, K.-B. *J. Am. Chem. Soc.* 108 (1986) 638; (k) Bays, J. P., Blumer, S. T., Baral-Tosh, S., Behar, D. and Neta, P. *J. Am. Chem. Soc.* 105 (1983) 320; (l) Behar, D. and Neta, P. *J. Am. Chem. Soc.* 103 (1981) 103; (m) Kochi, J. K. *Organometallic Mechanisms and Catalysis*, Academic Press, New York 1978.
- (a) von Stackelberg, M. and Stracke, W. *Z. Elektrochem.* 53 (1949) 118; (b) Casanova, J. and Ebersson, L. *The Chemistry of the Carbon-Halogen Bond*, Wiley, New York 1973, p. 979.
- Mishra, S. P. and Symons, M. C. R. *J. Chem. Soc., Chem. Commun.* (1973) 577; Brickenstein, E. Kh. and Khairutdinov, R. F. *Chem. Phys. Lett.* 115 (1982) 176.
- Symons, M. C. R. and Smith, I. G. *J. Chem. Soc., Faraday Trans. 1*, 81 (1985) 1095.
- (a) Ebersson, L. *Adv. Free Radical Biol. Med.* 1 (1985) 19; (b) For recent reviews, see Reynolds, E. S. and Moslen, M. T. *Liver: Norm. Funct. Dis.* 2 (1980) (Toxic Inj. Liver, Pt B) 541; Reynolds, E. S. and Moslen, M. T. *Free Radicals in Biology*, Vol. IV, p. 49; Recknagel, R. O. *Life Sciences* 33 (1983) 401.
- (a) Herberich, G. E. and Schwarzer, J. *J. Organometal. Chem.* 34 (1972) C43; (b) Willputte-Steinert, L. *Transition Met. Chem.* 3 (1978) 172; (c) Espenson, J. H. and McDowell, M. S. *Organometallics* 1 (1982) 1514; (d) Bamford, C. H. and Sakamoto, I. *J. Chem. Soc., Faraday Trans. 1*, 70 (1974) 330; (e) Bamford, C. H., Eastmond, G. C. and Fildes, F. J. T. *J. Chem. Soc., Chem. Commun.* (1970) 146; (f) Coper, T. A. *J. Am. Chem. Soc.* 95 (1973) 4158; (g) Strunkina, L. I. and Brainina, E. M. *Izv. Akad. Nauk. SSSR, Ser. Khim.* (1983) 2160; (h) Bagdasaryan, A. K., Zhakaryan, A. A., Bondarenko, G. N., Makovetskii, K. L. and Dolgoplosk, B. A. *Dokl. Akad. Nauk. SSSR* 275 (1984) 376; (i) Katz, S., Weiher, J. F. and Voigt, A. F. *J. Am. Chem. Soc.* 80 (1958) 6459; (j) El Murr, N. and Laviron, E. *Can. J. Chem.* 54 (1976) 3350.
- (a) Carpenter, W. *J. Org. Chem.* 30 (1965) 3082; (b) Sosonkin, I. M., Kalb, G. L. and Murev, V. P. *Dokl. Akad. Nauk. SSSR* 270 (1983) 340; (c) Limatibul, S. and Watson, J. W. *J. Org. Chem.* 37 (1972) 4491; (d) Wakselman, C. and Tordeux, M. *J. Org. Chem.* 50 (1985) 4047; (e) Rico, I., Cantacuzène, D. and Wakselman, C. *J. Org. Chem.* 48 (1983) 1979.
- Roberts, J. L., Jr., Calderwood, T. S. and Sawyer, D. T. *J. Am. Chem. Soc.* 105 (1983) 7691.
- (a) Mönig, J., Asmus, K.-D., Schaeffer, M., Slater, T. F. and Willson, R. L. *J. Chem. Soc., Perkin Trans. 2* (1983) 1133; (b) Mönig, J. and Asmus, K.-D. *J. Chem. Soc., Perkin Trans. 2* (1984) 2057.
- Ebersson, L. *J. Am. Chem. Soc.* 105 (1983) 3192.

11. For a recent review, see: Pope, M. T. *Heteropoly and Isopoly Oxometalates*, Springer-Verlag, Berlin and Heidelberg 1983.
12. Creaser, I. I., Harrowfield, J. Mac B., Herlt, A. J., Sargeson, A. M., Springborg, J., Geue, R. J. and Snow, M. R. *J. Am. Chem. Soc.* 99 (1977) 3181.
13. (a) Creaser, I. I., Sargeson, A. M. and Zanella, A. W. *Inorg. Chem.* 22 (1983) 4022; (b) Dubs, R. V., Gahan, L. R. and Sargeson, A. M. *Inorg. Chem.* 22 (1983) 2523.
14. Rudgewick-Brown, N. and Cannon, R. D. *J. Chem. Soc., Dalton Trans.* (1984) 479.
15. Creaser, I. I., Geue, R. I., Harrowfield, J. MacB., Herlt, A. J., Sargeson, A. M. and Springborg, J. *J. Am. Chem. Soc.* 104 (1982) 6016.
16. Lundberg, A. and Wickberg, B. *Proc. 20th Symposium on the Art of Glassblowing*, The American Glassblowers Society, Philadelphia 1975, p. 87.
17. Marquart, D. *J. Soc. Ind. Appl. Math.* 11 (1963). The program was purchased from Hewlett-Packard Co.
18. Hammerich, O. and Parker, V. D. *J. Chem. Soc., Perkin Trans. 1* (1972) 1718.
19. See, e.g., Lowry, T. H. and Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed., Harper & Row, New York 1981, Chap. 3.
20. Goodall, D. M. and Hardy, M. J. *J. Chem. Soc., Chem. Commun.* (1975) 919.
21. Jordan, F. *J. Phys. Chem.* 77 (1973) 2681.
22. El-Harakany, A. A., Sabet, V. M. and Sadek, H. *Z. Phys. Chem. Neue Folge* 97 (1975) 225.
23. (a) Meyers, W. C. *J. Phys. Chem.* 74 (1970) 2127; (b) Udachin, Y. M., Artamonova, N. N., Volkov, A. F., Lebedeva, A. S. and Guryanova, E. N. *J. Appl. Spectrosc.* 29 (1978) 812; (c) Mohan, H., Rao, K. N. and Iyer, R. M. *Indian J. Chem.* 22A (1983) 316; (d) Dumas, J. M., Peurichard, H. and Gomel, M. *J. Chem. Res. (S)* (1978) 54; (e) Dumas, J. M., Geron, C., Peurichard, H. and Gomel, M. *Bull. Soc. Chim. Fr.* (1976) 722.
24. Jönsson, L. *Unpublished results.*
25. (a) Effenberger, F., Podszun, W., Schoeller, W. W., Seufert, W. G. and Stohrer, W.-D. *Chem. Ber.* 109 (1976) 306; (b) Creighton, J. A. and Thomas, K. M. *J. Chem. Soc., Dalton Trans.* (1972) 2254.
26. Douchéret, G. and Morénas, M. *C.R. Seances Acad. Sci. Ser. C* (Paris) 264 (1967) 729.
27. Unger, F. D. *Thesis*, Georgetown University, Washington D.C. 1978; Kender, D. N. *Thesis*, Georgetown University, Washington D.C. 1975.
28. Rampi Scandola, M. A., Scandola, F. and Indelli, A. *J. Chem. Soc., Faraday Trans. 1*, 81 (1985) 2967.
29. Ebersson, L., Barry, J. E., Finkelstein, N., Moore, H. and Ross, S. D. *Acta Chem. Scand., Ser. B* 40 (1986) 283.

Received September 4, 1986