

# Electron Transfer Reactions in Organic Chemistry. XIII.\* The Reaction between Carbon Tetrabromide and the Heteropoly Blues $\text{Co(II)W}_{12}\text{O}_{40}^{7-}$ and $\text{Co(II)W}_{12}\text{O}_{40}^{8-}$ . A Kinetic and Product Study

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The reaction between carbon tetrabromide and  $\text{Co(II)W}_{12}\text{O}_{40}^{7-}$  was investigated at 20°C in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (64/36 v/v) buffered at pH ~ 7. It was found to be first-order in both substrate and reagent, the rate-determining step being an outer-sphere electron transfer reaction. The rate constant was determined to be  $1.1 \pm 0.3 \text{ M}^{-1} \text{ s}^{-1}$ . The only products found were  $\text{CHBr}_3$  (77 %) and  $\text{C}_2\text{Br}_6$  (1 %). Product studies in  $\text{CH}_3\text{CN}/\text{D}_2\text{O}$  showed that almost all of the tribromomethyl radical formed in the first step was further reduced to the corresponding anion. The rate constant for this reaction was estimated to be  $10^6 \text{ M}^{-1} \text{ s}^{-1}$ . The effect of inert salts on the overall reaction rate was also investigated. Tetraalkylammonium salts were found to augment the rate while alkali metal ions lowered it, which is the opposite of results with heteropoly ions as oxidants. The reaction between  $\text{CBr}_4$  and  $\text{Co(II)W}_{12}\text{O}_{40}^{8-}$  was first-order in heteropoly blue and if it was assumed it was first-order in  $\text{CBr}_4$  also, the rate constant could be calculated to be  $4.3 \text{ M}^{-1} \text{ s}^{-1}$ .

The possibility of electron transfer (ET) mechanisms in the reduction of organic halides has been much discussed in the literature.<sup>1</sup> More specifically, polyhalogenated aliphatics have been reduced with various reagents,<sup>2</sup> and some of the reactions have been claimed to proceed through an ET mechanism. We have turned our attention to these compounds as they should be more easily reduced than simple aliphatic halides.<sup>3</sup> It is believed that they might form stable anion radicals,<sup>4</sup> in contrast to monohalides.<sup>5</sup> Our interest in these compounds also originates from their well-known long-term toxicity,<sup>6</sup> which at least for carbon tetrachloride has been shown to be an effect of its ET reactivity.

In a previous study on the reduction of carbon tetrabromide by the cage complex  $\text{Co(II)sepulchrate}^{2+}$ ,<sup>7</sup> we attempted to define conditions un-

der which outer-sphere ET reduction of polyhalogenated aliphatics was feasible. This should be carried out using reagents which in principle are capable of reacting *via* outer-sphere ET only, as proved to be the case for  $\text{Co(II)sep}^{2+}$ . In this study we extend the investigation to the title reagents, still using carbon tetrabromide as pilot compound.

Heteropoly ions (for a recent review, see Ref. 8), such as 12-molybdates and -tungstates with a central metal ion surrounded by  $\text{MoO}_6$  or  $\text{WO}_6$  octahedra (Fig. 1, the Keggin structure), are generally recognized as being outer-sphere ET reagents, and have been used to investigate ET oxidations of organic compounds.<sup>9</sup> Less well-known are the so-called heteropoly blues (for reviews, see Ref. 10). These are obtained upon reduction of the heteropoly ions beyond the normal oxidation states of the central ion. The resulting species possess an intense blue colour from which they derive their name. The electrons

\*Part XII, see Ref. 26.

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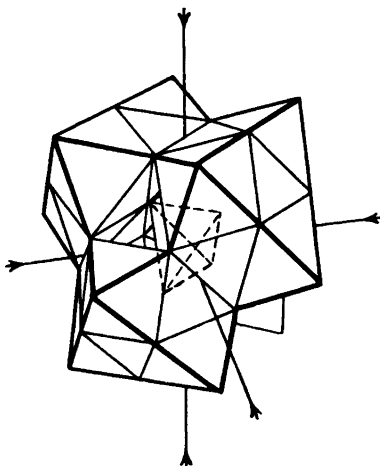


Fig. 1. Structure of the 12-tungstocobaltate(II) ion (the Keggin structure). The Co(II) ion is situated in the center of the tetrahedron and the tungsten atoms are situated in the octahedron centers. Each corner of an octahedron represents an oxygen atom.

are added to the tungstate or molybdate shell, and are weakly trapped on the individual metal atoms. The electrons are, however, spread over the whole shell by hopping between the metal atoms. If two electrons are added to the shell they are spin-paired but evenly distributed over the shell and not involved in bond formation, just as in the one-electron case. This can be seen as a very small structural change in going from the parent compound to the heteropoly blue. Even though the electrons are attached to the shell, each tungsten atom is still substitutionally inert.<sup>11</sup> Furthermore, the oxygen atoms exposed to the solution are non-basic and therefore unreactive.

We have used the 12-tungstocobaltate  $K_5HCo(II)W_{12}O_{40}$  (abbreviated  $CoW^{6-}$ ) as a parent compound for generating heteropoly blue reagents. At sufficiently high pH, as discussed below, it is possible by controlled potential electrolysis to form the one- and two-electron heteropoly blues  $Co(II)W_{12}O_{40}^{7-}$  ( $CoW^{7-}$ ) and  $Co(II)W_{12}O_{40}^{8-}$  ( $CoW^{8-}$ ), respectively. In most cases, the general observations regarding heteropoly blues discussed above have been directly confirmed for these compounds.<sup>12</sup>

## Experimental

**Chemicals.**  $K_5HCo(II)W_{12}O_{40} \cdot 15H_2O$  was prepared according to the literature procedure.<sup>13</sup> Carbon tetrabromide (Fluka *purum*) was sublimed at 70°C under reduced pressure. Doubly quartz-distilled water was used throughout.  $D_2O$  was from Ciba-Geigy and of 99.8% isotopic purity. Acetonitrile was either Baker HPLC or Riedel Pestanal quality and was used without further purification. All other chemicals were of highest commercial purity and were used as received.

**Preparation of the heteropoly blues and  $CBr_4$  solutions.** The procedures, glassware and electrochemical equipment used for preparing, transferring and storing the air-sensitive solutions of heteropoly blues were essentially the same as those previously described for the handling of  $\{Co(II) \text{ sepulchrate}^{2+}\}$  solution.<sup>12</sup> Throughout all experiments, care was taken not to expose the  $CBr_4$  solutions to light.

**Product studies.** Ten ml of a solution of 10 mM  $CoW^{6-}$ , 10 mM  $NaClO_4$  and 14 mM TRIS [=tris(hydroxymethyl)aminomethane] in water were reduced with 0.9 F per mol of  $CoW^{6-}$ . The anolyte and middle cell solution were 10 mM  $NaClO_4$ , 14 mM TRIS, 10 mM  $HClO_4$  and 25 mM  $KClO_4$ . The catholyte was then added to a stirred solution (40 ml) of 5 mM  $CBr_4$  in 50%  $CH_3CN/H_2O$ . The reaction mixture was left at room temperature for about 2 h, after which water (ca. 20 ml) was added and the resulting mixture was extracted with 3×5 ml of  $CH_2Cl_2$ . The combined organic phases were washed twice with water, dried with  $MgSO_4$  and filtered. Due to the volatility of the polyhalo compounds, about 1 ml of the filtrate was saved for quantitative analysis. The rest was gently evaporated to 1 ml, examined for trace products and used for GLC/MS analysis. A product study with  $H_2O$  replaced by  $D_2O$  was performed in exactly the same way. The GLC analysis was performed on a Varian 3300 chromatograph equipped with a J&W DB-115 m Megabore column and a flame-ionization detector. A Finnigan 4021 mass spectrometer operating at 19 eV was used for the GLC/MS analysis. This was used to analyze the product runs in  $CH_3CN/D_2O$ . The important peaks for the determination of the two products found were  $m/z$  (% rel. int.):  $CDBr_3$ : 257(1), 255(4), 253(4), 251(1),

176(45), 174(100) and 172(53);  $C_2Br_6$ : 348(1), 346(3), 344(5), 342(3) and 340(1).

**Kinetics.** All kinetic measurements were made at 20.0°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. Two ml of a solution of 80%  $CH_3CN/H_2O$  with  $CBr_4$  and added salt were thermally equilibrated in the cell compartment. To this solution was added 0.5 ml of the following solution in water: 1 mM  $CoW^{6-}$  reduced with 0.9 F per mol (at  $-0.8$  V vs. 10 mM  $Ag/NaClO_4$ ,  $H_2O$  for the  $CoW^{7-}$  experiments, and at  $-0.9$  V for the  $CoW^{8-}$  experiments), 10 mM  $NaClO_4$ , 5 mM TRIS, 3.5 mM  $HClO_4$ . The kinetics were monitored at 640 and 620 nm, respectively, 200 data points being automatically collected at regular intervals and stored on magnetic tape. The data set could then be analyzed on an HP-9835 table-top computer by the non-linear regression method developed by Marquardt.<sup>14</sup>

**UV/VIS spectra.** The solutions used for recording the UV/VIS spectra were mixed in the same way, and recorded with the same apparatus and under the same conditions as in the kinetic measurements. The resulting spectral data were stored on magnetic tape, thus making it possible to add/subtract spectra from different recordings (see Results).

**Cyclic voltammetry.** CV was performed with a BAS-100 electrochemical analyzer at  $\sim 20^\circ C$ . The working electrode was an Au disc, amalgamated with triply-distilled Hg. The reference electrode was either an  $Ag/AgCl$  electrode, or the previously mentioned  $Ag/H_2O$ ,  $NaClO_4$ . A Pt wire was used as counter electrode.

## Results

**Preparation of the heteropoly blue solution.** When stirring the pale blue  $CoW^{6-}$  solution in contact with an Hg cathode without electrolysis, the solutions often became cloudy and a precipitate was sometimes formed. Upon reduction to  $CoW^{7-}$  the solution became clear again; this was not tried if the precipitate was formed. Toward the end of the investigation we found that if the solution was first deaerated outside the cell (i.e., not in contact with Hg) and thereafter transferred

to the cathode compartment with immediate onset of the electrolysis, the phenomenon could be completely avoided. Check experiments with these solutions showed no significant deviations from the kinetics reported here.

**Product studies.** The product studies were performed in 40% instead of 64% acetonitrile for solubility reasons. Otherwise the conditions were very similar (see Experimental). The only products found were  $CHBr_3$  and  $C_2Br_6$ . When the reaction was run in  $CH_3CN/D_2O$  the bromoform was 99% deuteriated. From these runs the products were identified by their mass spectra, which could be compared with the mass spectra of authentic specimens. The  $CDBr_3/CHBr_3$  ratio was determined from the mass spectra by comparing the relative intensities of the four  $CDBr_3$  peaks at  $m/z$  257, 255, 253 and 251 with the four  $CHBr_3^+$  peaks at  $m/z$  256, 254, 252 and 250. Thus, the yields as determined from four runs, calculated on the basis of a consumption of 2 mol of  $CoW^{7-}$  per mol of  $CHBr_3$  or per mol of  $C_2Br_6$ , were:  $CHBr_3$ , 77% and  $C_2Br_6$ , 1%. Losses due to less than 100% current efficiency in the reduction of  $CoW^{6-}$ , or possible  $O_2$  reaction with  $CoW^{7-}$  were not accounted for. The low yield of  $C_2Br_6$ , together with its not altogether perfect mass spectrum, led us to perform a control experiment. All the organic chemicals known to be present under work-up conditions (except  $C_2Br_6$ ) were mixed in a vessel and irradiated with artificial laboratory light for about 1 h. Neither before nor after concentration by evaporation could any  $C_2Br_6$  be detected (GLC). This shows that the  $C_2Br_6$  detected in the product runs was not formed in any uncontrolled photochemical reaction.

**Cyclic voltammetry.** The shape of the CV waves for  $CoW^{6-}$  turned out to be dependent on the concentration of both  $CoW^{6-}$  and the electrolyte salt, as well as on the electrode material. Thus, initial attempts to use glassy carbon as the working electrode failed completely since the electrode strongly and irreversibly adsorbed the reduced heteropoly ion and thereafter gave rise only to catalytic waves for water reduction. This phenomenon has already been described for other heteropoly anions<sup>15</sup> and will not be considered here. An Hg/Au electrode which was never taken beyond  $-1.2$  V vs.  $Ag/AgCl$  did not give rise to these problems. The main features found

Table 1. Electrochemical measurements of the reduction of  $\text{CoW}^{6-}$ . All potentials vs. NHE. Scan rate =  $10 \text{ mV s}^{-1}$ .

Entry	Conditions	1st wave			2nd wave			Ref.
		$-E^{\circ}/\text{mV}^a$	$\Delta E/\text{mV}^b$	$n^c$	$-E^{\circ}/\text{mV}^a$	$\Delta E/\text{mV}^b$	$n^c$	
1	$\text{H}_2\text{O}$ , 1 M sulfate, $\text{pH} \geq 5.4$	270		1	470		1	12a
2	$\text{H}_2\text{O}$ , 1 M sulfate, $\text{pH} 2.4$	260		2	400		2	12a
3	$\text{H}_2\text{O}$ , 0.1 M $\text{NaClO}_4$ , $\text{pH} 7^d$	351	80	1	548	61	1	This work
4	$\text{H}_2\text{O}$ , 0.1 M $\text{NaClO}_4$ , $\text{pH} 2^e$	361	81	2	557	66	2	This work
5	64% $\text{CH}_3\text{CN}$ , 0.1 M $\text{NaClO}_4$ , $\text{pH} 7^d$	439	—	1	517	42	1	This work
6	64% $\text{CH}_3\text{CN}$ , 0.1 M $\text{NaClO}_4$ , $\text{pH} 2^e$	226	51	2	332	43	2	This work
7	64% $\text{CH}_3\text{CN}$ , 0.1 M $\text{Me}_4\text{NClO}_4$ , $\text{pH} 7^d$	485	132	1	660	113	1	This work

<sup>a</sup> $(E_{\text{anodic peak}} + E_{\text{cathodic peak}})/2$ . <sup>b</sup> $E_{\text{anodic peak}} - E_{\text{cathodic peak}}$ . <sup>c</sup>Number of electrons. <sup>d</sup>Buffered with  $\text{TRIS}/\text{HClO}_4 + \text{CoW}^{6-}$ . <sup>e</sup>Only  $\text{HClO}_4$  and  $\text{CoW}^{6-}$ .

in the reduction of  $\text{CoW}^{6-}$  in 64%  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  are the same as those described for  $\text{CoW}^{6-}$  in 1 M aqueous solutions of  $\text{H}_2\text{SO}_4/\text{Na}_2\text{SO}_4$ <sup>12a</sup> (Table 1, entries 1 and 2). Thus, at low pH two two-electron reduction waves were found, and in neutral solution the first wave split into two one-electron waves. We made no attempt to characterize the second two-electron wave in neutral solution.

In neutral aqueous 0.1 M  $\text{NaClO}_4$  solution the two one-electron waves were separated by 200

mV, the same value as for 1 M sulfate solution, but both waves were slightly cathodically shifted (Table 1, entries 3 and 4). It was found to be impossible to characterize the reduction of  $\text{CoW}^{6-}$  in neutral 64%  $\text{CH}_3\text{CN}$  solutions when only 10 mM  $\text{NaClO}_4$  (i.e. the concentration used in the electrolysis) was used as electrolyte because no anodic waves were seen. Upon raising  $[\text{NaClO}_4]$  to 100 mM, two distinct anodic waves appeared; however, the shape and size of the cathodic waves remained practically unchanged (Fig. 2a). Keeping  $[\text{NaClO}_4]$  at 100 mM while raising  $[\text{CoW}^{6-}]$  from 0.5 to 2 mM, the first cathodic wave disappeared while the corresponding anodic wave became more pronounced. These results can probably be attributed to adsorption/desorption phenomena similar to those observed at the glassy carbon electrode.

In neutral solution the potentials for both the reductions were shifted in the cathodic direction when the electrolyte was changed from 0.1 M  $\text{NaClO}_4$  to 0.1 M  $\text{Me}_4\text{NClO}_4$ . The separation between the potentials also increased, while the reversibility decreased (Table 1, entries 5 and 7; Fig. 2b). The  $E_{1/2}$  values listed in Table 1 were calculated as the arithmetic mean of the potentials of the cathodic and anodic waves, except for the first wave in entry 5, where the shape of the first cathodic wave precluded this. Instead, this was calculated as  $E_{1/2}$  for the second wave minus the difference between the peak potentials of the anodic waves, i.e. as in eqn. (1).

$$E_{1/2} = (E_{\text{pa},2\text{nd}} + E_{\text{pc},2\text{nd}})/2 - (E_{\text{pc},2\text{nd}} - E_{\text{pc},1\text{st}}) \quad (1)$$

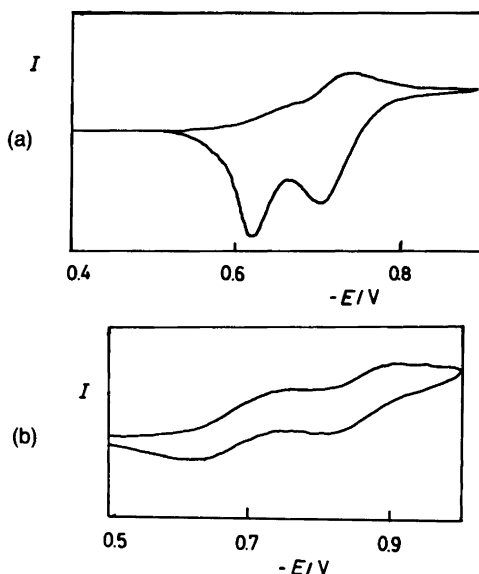


Fig. 2. CV of  $\text{CoW}^{6-}$ . Experimental conditions: see Table 1, except for  $E$  which is given vs.  $\text{Ag}/\text{AgCl}$ . (a)  $\text{NaClO}_4$  as electrolyte (Table 1, entry 5). (b)  $\text{Me}_4\text{NClO}_4$  as electrolyte (Table 1, entry 7).

*UV/VIS spectra.* We recorded spectra after having reduced  $\text{CoW}^{6-}$  with 0, 0.5, 0.75, 1.0, 1.5 and 2.0 F per mol (Fig. 3a). If we look at the part of the spectra corresponding to 700–800 nm it can be seen that the spectrum obtained at 1.0 F per mol  $\text{CoW}^{6-}$  has a different shape (slightly convex) than that for 2.0 F per mol  $\text{CoW}^{6-}$  (concave), which is assumed to be that of  $\text{CoW}^{8-}$ . At these wavelengths  $\text{CoW}^{6-}$  does not absorb at all (0 F per mol  $\text{CoW}^{6-}$ ) and there is thus no way to add the  $\text{CoW}^{6-}$  and  $\text{CoW}^{8-}$  spectra to obtain that for 1.0 F per mol  $\text{CoW}^{7-}$ . This means that the latter cannot be attributed to any concentration of  $\text{CoW}^{8-}$  and instead must largely (see below) be regarded as the spectrum of an intermediate species, namely  $\text{CoW}^{7-}$ .

We also tried to see whether the first F per mol introduced led to quantitative  $\text{CoW}^{7-}$ , or whether an equilibrium according to eqn. (2) was attained. The relative concentrations of  $\text{CoW}^{6-}$ ,



$\text{CoW}^{7-}$  and  $\text{CoW}^{8-}$  in 64%  $\text{CH}_3\text{CN}$  with 100 mM  $\text{NaClO}_4$  as electrolyte (Table 2), were calculated using  $K_{\text{eq}}$  for eqn. (2), known from the electrochemical experiments. We thereafter treated the spectra recorded after 0.5, 0.75 and 1.0 F per mol  $\text{CoW}^{7-}$  so as to give the component deriving from  $\text{CoW}^{7-}$  alone. For example, at 1.0 F per mol the non-equilibrium model predicted that the recorded spectrum is simply the spectrum of  $\text{CoW}^{7-}$ , while use of the equilibrium model required that the parts of the spectrum contributed by  $\text{CoW}^{6-}$  and  $\text{CoW}^{8-}$  had to be subtracted in order to obtain the pure spectrum of  $\text{CoW}^{7-}$ . These calculations gave two series of spectra assumed to be those of  $\text{CoW}^{7-}$ , one for the equilibrium and one

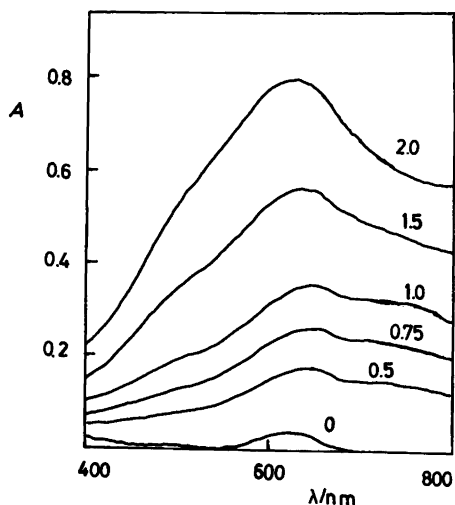


Fig. 3. UV spectrum of  $\text{CoW}^{6-}$  reduced with 0–2 F per mol  $\text{CoW}^{8-}$ . Experimental conditions: 0.2 mM  $\text{CoW}^{6-}$ , 2.0 mM  $\text{NaClO}_4$ , 1.0 mM TRIS, 0.7 mM  $\text{HClO}_4$ ,  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (64/36 v/v), 20 °C.

for the non-equilibrium model. If one of the models were correct one would ideally obtain three identical spectra. It turned out that the models gave very similar results. For example at 1.0 F per mol  $\text{CoW}^{6-}$  we obtain: non-equilibrium model  $\lambda_{\text{max}} = 654 \text{ nm}$ ,  $\epsilon = 1790 \text{ M}^{-1} \text{ cm}^{-1}$ ; equilibrium model  $\lambda_{\text{max}} = 654 \text{ nm}$ ,  $\epsilon = 1690 \text{ M}^{-1} \text{ cm}^{-1}$ , which means that even at the wavelength where the models are supposed to differ maximally, the difference is within the limits of experimental error (see below).

If we despite this (see Discussion) accept the spectra for 1 F per mol and 2 F per mol as being the spectra of  $\text{CoW}^{7-}$  and  $\text{CoW}^{8-}$ , respectively,

Table 2. Relative concentrations of  $\text{CoW}^{6-}$ ,  $\text{CoW}^{7-}$  and  $\text{CoW}^{8-}$  in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (64/36) at pH ~ 7, 0.1 M  $\text{NaClO}_4$  as a function of number of F per mol of  $\text{CoW}^{6-}$  if an equilibrium according to eqn. (2) is obtained (non-equilibrium model results in parentheses).

F per mol $\text{CoW}^{6-}$	$\text{CoW}^{6-}$	$\text{CoW}^{7-}$	$\text{CoW}^{8-}$
0	1 (1)	0 (0)	0 (0)
0.5	0.52 (0.5)	0.46 (0.5)	0.02 (0)
0.75	0.31 (0.25)	0.63 (0.75)	0.06 (0)
1.0	0.15 (0)	0.70 (1)	0.15 (0)
1.5	0.02 (0)	0.46 (0.5)	0.52 (0.5)
2.0	0 (0)	0 (0)	1 (1)

we obtain for  $\text{CoW}^{7-}$ :  $\lambda_{\text{max}} = 650 \pm 10 \text{ nm}$  and  $\epsilon_{650} = 1700 \pm 100 \text{ M}^{-1} \text{ cm}^{-1}$ , and for  $\text{CoW}^{8-}$ :  $\lambda_{\text{max}} = 628 \pm 5 \text{ nm}$ ,  $\epsilon_{628} = 3800 \pm 400 \text{ M}^{-1} \text{ cm}^{-1}$ .

*Kinetics.* All kinetic runs were made at  $20.0 \pm 0.1^\circ \text{C}$  and followed by monitoring the disappearance of the heteropoly blue at 640 nm (620 nm for  $\text{CoW}^{8-}$ ). All runs were performed under pseudo-first order conditions, the  $\text{CBr}_4$ /heteropoly blue ratio never being less than 8. The observed rate constants were calculated by fitting the data to eqn. (3) using  $A_\infty$  and  $k_{\text{obs}}$  as the

$$A = A_\infty + (A_0 - A_\infty) \exp(-k_{\text{obs}} t) \quad (3)$$

adjustable parameters ( $A$  denotes absorbance).  $A_0$  was taken directly from the experiments. An effort to use the same equation but with  $A_0$  as the third adjustable parameter gave very similar constants, so this extra complexity could not be justified. The experimentally found  $A_\infty$  and the  $A_\infty$  anticipated from the known absorptivity of  $\text{CoW}^{6-}$  were found to be in reasonable agreement ( $\pm 0.01$  absorbance units). When checked, the spectrum of  $\text{CoW}^{6-}$  was always obtained after

Table 3. Variation of  $k_{\text{obs}}$  with  $[\text{CBr}_4]$  and electrolyte salts.  $[\text{CoW}^{7-}] \sim 0.2 \text{ mM}$ ,  $\text{pH } 7$ ,  $^\circ [\text{TRIS}] = 1 \text{ mM}$ ,  $[\text{HClO}_4] = 0.70 \text{ mM}$ .

Entry	$[\text{CBr}_4]/\text{mM}$	[Electrolyte]/mM	$\text{CH}_3\text{CN}/\text{vol } \%$	$k_{\text{obs}}/\text{min}^{-1}$	
1 <sup>a</sup>	5.2 <sup>a</sup>	$\text{NaClO}_4$	2.0 <sup>a</sup>	40 <sup>a</sup>	0.93 <sup>a</sup>
2	1.6	"	2.0	64	0.22
	2.8	"	2.0	64	0.37
	5.2	"	2.0	64	0.78
	8.8	"	2.0	64	1.12
6	16	"	2.0	64	2.13
7	5.2	"	1.0	64	0.67
	"	"	2.0	64	0.64
	"	"	5.0	64	0.59
	"	"	6.0	64	0.54
	"	"	8.1	64	0.63
	"	"	9.1	64	0.56
	"	"	12.3	64	0.51
	"	"	23	64	0.40
	"	"	42	64	0.41
	"	"	102	64	0.24
17	"	"	208	64	0.16
18	2.0	$\text{Me}_4\text{NClO}_4$	0 <sup>b</sup>	64	0.22
	"	"	5.1 <sup>b</sup>	64	0.56
	"	"	10 <sup>b</sup>	64	0.70
	"	"	20.4 <sup>b</sup>	64	0.81
	"	"	51 <sup>b</sup>	64	1.19
23	"	"	101 <sup>b</sup>	64	1.40
24	5.2	$\text{LiClO}_4$	10.4 <sup>b</sup>	64	0.49
25	"	$\text{NaClO}_4$	10.4 <sup>b</sup>	64	0.51
26	"	$\text{LiClO}_4$	207 <sup>b</sup>	64	0.21
27	"	$\text{NaClO}_4$	206 <sup>b</sup>	64	0.16
28	"	$\text{LiBF}_4$	10 <sup>b</sup>	40	1.04
29	"	$\text{KBF}_4$	10 <sup>b</sup>	40	0.73
30	"	$\text{CsBF}_4$	10 <sup>b</sup>	40	0.55
31	"	$\text{Me}_4\text{NClO}_4$	10 <sup>b</sup>	64	1.50
32	"	$\text{Bu}_4\text{NClO}_4$	10 <sup>b</sup>	64	1.12
33	"	$\text{LiClO}_4$	10 <sup>b</sup>	64	0.50
34 <sup>d</sup>	1.9 <sup>d</sup>	$\text{NaClO}_4$	2.0 <sup>d</sup>	64 <sup>d</sup>	0.49 <sup>d</sup>

<sup>a</sup>Also added:  $[\text{CoW}^{6-}] = 0.9 \text{ mM}$ ,  $[\text{NaOH}] = 0.9 \text{ mM}$ . <sup>b</sup>Also  $[\text{NaClO}_4] = 2 \text{ mM}$ . <sup>c</sup>See Ref. 12. Furthermore,  $\text{K}_5\text{HCo(II)W}_{12}\text{O}_{40}$  is a strong acid. <sup>d</sup> $\text{CoW}^{8-}$  instead of  $\text{CoW}^{7-}$ .

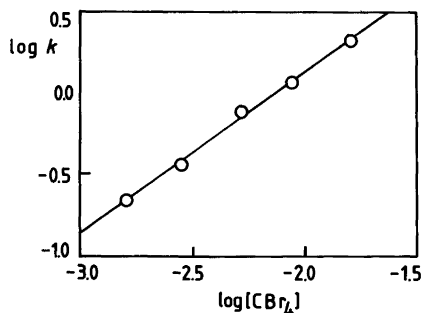


Fig. 4. Plot of  $\log (k_{\text{obs}}/\text{min}^{-1})$  vs.  $\log ([\text{CBr}_4]_0/\text{M})$ .

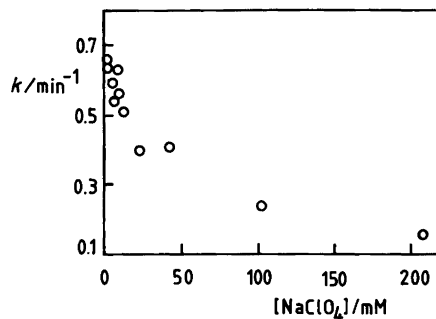


Fig. 5. Plot of  $k_{\text{obs}}$  vs.  $[\text{NaClO}_4]$ .

the reaction was complete. The first ten data pairs (corresponding to somewhat less than one half-life) were discarded in most of the runs. Data for at least three half-lives were used for all the calculations.

For a few runs which were fitted badly by eqn. (3) when using the whole data set, a three parameter equation allowing for the back ET reaction<sup>9</sup> between  $\text{CBr}_4^{\cdot-}$  and  $\text{CoW}^{6-}$  was tried. This treatment sometimes gave significantly better results, indicating a possible back ET reaction. However, the addition of extra  $\text{CoW}^{6-}$  to the reaction mixture (Table 3, entry 1) did not slow down the reaction more than expected from the salt effect (see below), and in these experiments a good fit was obtained with eqn. (3).

**Reaction order.** The reaction order in  $\text{CBr}_4$  was determined by varying the concentration of  $\text{CBr}_4$  and plotting  $\log k_{\text{obs}}$  vs.  $\log [\text{CBr}_4]$  (Table 3, entries 2–6; Fig. 4). The linear plot gave a slope of 1.00, which shows the reaction to be first-order in  $\text{CBr}_4$ . To obtain these rate constants it was found necessary to prepare all the  $\text{CBr}_4$  solutions of different concentrations by diluting a previously deaerated stock solution and subsequently protecting them from the atmosphere by passing a slow stream of argon over the solutions.

**pH.** When the reactions were performed in acidic medium, they were too slow to give a reliable rate constant. This was easily rationalised on the basis of the much lower reduction potential of the heteropoly blues in acidic solutions (Table 1).

**Effect of added  $\text{NaClO}_4$ .** The effect of varying the concentration of  $\text{NaClO}_4$  from 1 to 200 mM was investigated (Table 2, entries 7–17; Fig. 5). The

reproducibility of  $k_{\text{obs}}$  was rather poor for each  $[\text{NaClO}_4]$ , at worst  $\pm 20\%$ , but this could be explained as being the result of using different batches of deaerated  $\text{CBr}_4$  solution and heteropoly anion solution. Despite the scattered points at lower  $[\text{NaClO}_4]$  the trend is clear:  $\text{NaClO}_4$  retards the reaction but the retardation levels off at around  $[\text{NaClO}_4] = 100$  mM.

**Effect of added  $\text{Me}_4\text{NClO}_4$ .** When  $\text{Me}_4\text{NClO}_4$  was added, the opposite effect to that of  $\text{NaClO}_4$  was seen (Table 2, entries 18–23; Fig. 6). The reaction rate increased but the saturation effect at high electrolyte concentration was also seen here. The reproducibility was somewhat better, probably because fewer batches were used.

**Variation of the cation.** This was carried out in three series of runs (Table 2, entries 24–27, 28–30 and 31–33, respectively) because of solubility problems with  $\text{K}^+$  ions.  $\text{Li}^+$  was included in all the series, thereby making them comparable. Within each series the same batch of deaerated substrate and reagent solution was used. The following list of reaction rate enhancements at 0.01 M electrolyte concentration was obtained, the rate enhancement relative to  $\text{Li}^+$  being given in parentheses:  $\text{Me}_4\text{N}^+$  (3.0) >  $\text{Bu}_4\text{N}^+$  (2.2) >  $\text{Li}^+$  (1)  $\approx$   $\text{Na}^+$  (1) >  $\text{K}^+$  (0.7) >  $\text{Cs}$  (0.5). The final absorbance,  $A_\infty$ , obtained in the runs with  $\text{CsBF}_4$  was too high compared to the expected value of  $A_\infty = 0.04$ . This might be due to the formation of small amounts of a precipitate, with subsequent light scattering, and it did not seem to influence the kinetics.

**$\text{CoW}^{8-}$  and  $\text{CBr}_4$ .** A few kinetic runs were made with  $\text{CoW}^{8-}$  and  $\text{CBr}_4$  under the same conditions

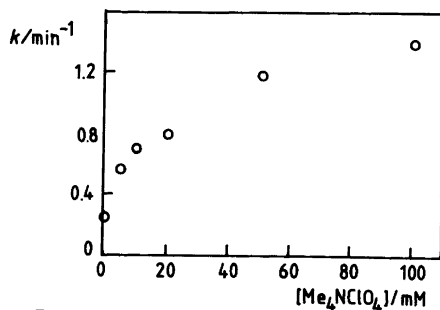


Fig. 6. Plot of  $k_{\text{obs}}$  vs.  $[\text{Me}_4\text{NClO}_4]$ .

as with  $\text{CoW}^{7-}$  (Table 2, entry 34). We found consistently good pseudo first-order kinetics, and thus no indication of any intermediate  $\text{CoW}^{7-}$  (see below). The observed rate constants was about twice the observed rate constant for the corresponding reaction with  $\text{CoW}^{7-}$ . The rate constant did not change if only the part of the curve corresponding to an absorbance  $< 0.21$  was used for the calculations. Following Scheme 2 (see Discussion) this would give  $k_{\text{ET}} = 4.3 \text{ M}^{-1} \text{ s}^{-1}$ . The spectrum of  $\text{CoW}^{6-}$  was obtained after completion of the reaction, although some baseline deviation was observed which was probably due to slight precipitation.

## Discussion

The somewhat complicated one- and two-electron electrochemistry makes it important to establish which heteropoly blue is the active one in our experiments. When  $\text{CoW}^{6-}$  is reduced in water at  $\text{pH} \sim 7$ , the difference of 200 mV between  $E^\circ$  for  $\text{CoW}^{6-/7-}$  and  $\text{CoW}^{7-/8-}$  is sufficient to guarantee that practically no  $\text{CoW}^{8-}$  is formed and that the equilibrium [eqn. (2)] is far to the left. Upon mixing the substrate and reagent solutions to give a solution of 64% AN the  $E^\circ$  between  $\text{CoW}^{6-/7-}$  and  $\text{CoW}^{7-/8-}$  is decreased to 80 mV; thermodynamically it would therefore be possible for  $\text{CoW}^{7-}$  to disproportionate to  $\text{CoW}^{6-}$  and  $\text{CoW}^{8-}$ , giving the concentrations shown in Table 2. Unfortunately the UV experiments did not show whether this happened or not. We can, however, estimate the rate constant for this reaction from the Marcus theory<sup>16,5</sup> for outer-sphere

ET reactions. In its simplest form, Marcus' theory describes  $\Delta G^\ddagger$  as a function of  $\Delta G^{\circ'}$ , i.e.  $\Delta G^\circ$  corrected for an electrostatic term, and  $\lambda$ , the reorganization energy [eqns. (4)–(7)]. The reorganization energy is the energy required for the reactants to reorganize their bond lengths, angles etc. and their solvation shell in order to be able to transfer the electron according to the Franck-Condon principle. The rate constant can then be calculated from the Eyring equation [eqn. (8)]:

$$\Delta G^\ddagger = W + \frac{\lambda}{4} \left( 1 + \frac{\Delta G^{\circ'}}{\lambda} \right)^2 \quad (4)$$

$$W = \frac{331.3 Z_1 Z_2 B}{D r_{12}} \quad (5)$$

$$\Delta G^{\circ'} = \frac{331.3 B}{D r_{12}} (Z_1 - Z_2 - 1) + \Delta G^\circ \quad (6)$$

$$B = 10^{-21.9} r_{12} (\mu D T)^{1/2} \quad (7)$$

$$k = 10^{11} e^{-\Delta G^\ddagger / RT} \quad (8)$$

Here,  $W$  is the electrostatic work required to bring the reactants together,  $Z_1$  and  $Z_2$  are the charges of the ions,  $D$  is the dielectric constant,  $r_{12}$  is the distance between the centers of the reactants, and  $\mu$  is the ionic strength. Eqns. (5)–(7) give the energies directly in  $\text{kcal mol}^{-1}$ .

If the reorganization energies for the self-exchange reactions for both donor [eqn. (9)] and acceptor [eqn. (10)] are known, the  $\lambda$  value for their cross reaction [eqn. (11)] is calculated from eqn. (12).

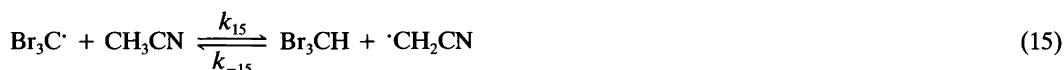
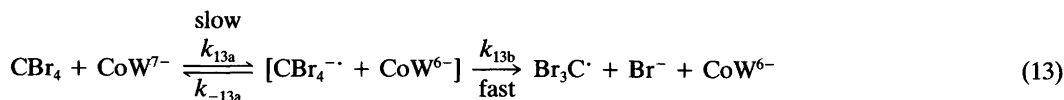


$$\frac{\lambda_{\text{D}} + \lambda_{\text{A}}}{2} = \lambda_{\text{DA}} \quad (12)$$

We can now return to our problem and note that the rate for the self-exchange reactions of the Keggin structure heteropoly blue  $\text{PW}_{12}\text{O}_{40}^{3-/4-}$

<sup>5</sup>For discussions of its application in organic chemistry and for references, see Ref. 17.





*Scheme 1.*

has been measured<sup>11</sup> and found to be  $10^7 \text{ M}^{-1} \text{ s}^{-1}$ , which is near the diffusion-controlled limit for these ions. This should mean that the  $\lambda$  value is very low, probably around  $10 \text{ kcal mol}^{-1}$ , similar to those of many organic molecules. We assume that this also holds for the  $\text{CoW}^{6-/7-}$  and  $\text{CoW}^{7-/8-}$  self-exchange reactions as the tungstate shells are the same here. Furthermore, this gives via eqns. (9)–(12), a value of  $\lambda = 10 \text{ kcal mol}^{-1}$  for the disproportionation of  $\text{CoW}^{7-}$ , and the electrochemical measurements give  $\Delta E^\circ = -80 \text{ mV}$  (Table 1, entry 5). We can now calculate the rate constant from eqns. (4)–(8) using the following parameters:  $Z_1 = Z_2 = -7$ ,  $D = 51.2$ ,\*  $r_{12} = 11.2 \text{ \AA}$  and  $\mu = 0.0083 \text{ M}$ . These values give  $\Delta G^\ddagger = 27.8 \text{ kcal mol}^{-1}$  and  $k_{\text{ET}} = 10^{-10} \text{ M}^{-1} \text{ s}^{-1}$ . Even if we assume that ion pairing makes the charges smaller we still obtain very low rate constants, and we are therefore convinced that no equilibrium is attained and thus no or very little  $\text{CoW}^{8-}$  is formed.

The kinetic and product studies indicate the mechanism for a reaction between  $\text{CBr}_4$  and  $\text{CoW}^{7-}$  in neutral solution given in Scheme 1. Scheme 1 accounts for the products formed and for the fact that  $\text{CoW}^{6-}$  was always recovered after completion of the reactions. The existence of any back ET reaction could also be refuted (see Results). Of course, this only proves that  $k_{13b} \gg k_{-13a}$  and thus cannot be taken as evidence against the possible existence of the carbon tetra-

bromide anion radical. The one per cent of non-deuteriated bromoform formed in the  $\text{CH}_3\text{CN}/\text{D}_2\text{O}$  product runs might be the result of contamination with  $\text{H}_2\text{O}$ , so we have no direct evidence for the occurrence of the  $\text{H}^\cdot$  abstraction reaction [eqn. (15)]. The product distribution also shows that we can neglect eqns. (14) and (15) in deriving the rate law for the reaction. Using the steady-state assumption for  $[\text{Br}_3\text{C}^\cdot]$  we arrive at eqn. (18).

$$\nu = 2 k_{\text{ET}} [\text{CBr}_4][\text{CoW}^{7-}] \quad (18)$$

This is in accordance with the first-order behaviour with respect to both  $\text{CBr}_4$  and  $\text{CoW}^{7-}$ . From the rate law and entries 2–7 in Table 3 we can calculate  $k_{\text{ET}} = 1.1 \pm 0.3 \text{ M}^{-1} \text{ s}^{-1}$ .

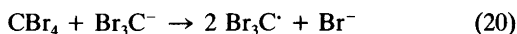
It is also possible to obtain rough estimates of  $k_{15}$  and  $k_{16}$ , provided the following assumptions are made: Firstly, the recombination rate for  $\text{Br}_3\text{C}^\cdot$  is equal to that for  $\text{Cl}_3\text{C}^\cdot$ , i.e.  $5 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>18</sup> Secondly, the steady-state approximation is valid for  $[\text{Br}_3\text{C}^\cdot]$  for the whole reaction time, i.e.,  $t$ , arbitrarily chosen as  $\sim 5$  half-lives, which is equal to 400 s. Thus, we obtain eqn. (19) from which  $[\text{Br}_3\text{C}^\cdot]$  can be found. It is now easy to calculate  $k_{15} \leq 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{16} = 10^6 \text{ M}^{-1} \text{ s}^{-1}$ .  $[\text{C}_2\text{Br}_6]_{\text{final}}$  in eqn. (19) is the concentration found in the product runs. It must be emphasized that

$$[\text{C}_2\text{Br}_6]_{\text{final}} = k_{13} [\text{Br}_3\text{C}^\cdot]^2 \cdot t \quad (19)$$

the formation of  $\text{Br}_3\text{C}^\cdot$  radicals in our system

\*This was calculated as in Ref. 7.

does not necessarily mean that they are formed as in eqn. (13). Instead, they could be formed according to eqn. (20). This possibility has been pointed out for similar systems.<sup>19</sup> In our case this reaction seems, however, to be less likely as we have employed rather low pH and the fast prot-



onation of the anion\* would be able to compete successfully with reaction (20) which must be endergonic as  $\text{Br}_3\text{C}^\cdot$  is easier to reduce than  $\text{CBr}_4$ . This would also imply that the tribromomethyl anion required in eqn. (20) would be formed in the reaction between  $\text{CBr}_4$  and  $\text{CoW}^{7-}$  through a polar mechanism, here a nucleophilic attack on a positive bromine. The only candidates for this attack are the oxygens on the tungstate shell, and since these are nearly inert (see Introduction), the reaction seems highly improbable.

Finally, it must be pointed out that the results and conclusions regarding the mechanism parallel those arrived at for the reaction between  $\text{CBr}_4$  and  $\text{Co(II)sep}^{2+}$  in our previous study.<sup>7</sup> In the latter study it was also shown that TRIS and  $\text{Br}^-$  present in the solution did not affect the kinetics by putative complexation with  $\text{CBr}_4$ .

In view of the high ionic charge of the reducing agent we also investigated the effect of inert salts on the reaction rate. The study was limited to varying the cation as it is the ions of opposite charge to those of the reactants that mainly determine the kinetic effect of the added salt.<sup>22</sup> Previous reports on the effects of salts on ET rates for reactions with heteropoly ion,<sup>9,23</sup> and for other systems,<sup>24</sup> have mainly dealt with the heteropoly ion as an oxidant. Here, the normal effect of variation of the cation has been increasing rates with alkali metal ions and decreasing rates with tetraalkylammonium salts. We find almost the opposite trend in our system, i.e. decreasing rates with alkali metal ions and increasing rates with tetraalkylammonium salt. Part of this effect can

be accounted for by the decrease in  $E_{1/2}$  of 50 mV seen in the CV experiments on going from 0.1 M  $\text{NaClO}_4$  to 0.1 M  $\text{Me}_4\text{NClO}_4$  as electrolyte. This is in line with the decrease in  $E^\circ$  for the  $\text{Co(III)W}_{12}\text{O}_{40}/\text{Co(II)W}_{12}\text{O}_{40}$ <sup>9a</sup> and  $\text{Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{2-}$ <sup>24a</sup> couples with the same change of electrolyte. However, using reasonable values for  $\text{CBr}_4$  as oxidant [ $E^\circ = -0.6$  V and  $\lambda = 60$  kcal mol<sup>-1</sup>]<sup>8</sup> we can calculate from eqns. (4)–(8) and (11) that a decrease in  $E_i$  of 50 mV would give a rate acceleration by a factor of only 3, while experimentally we find a factor of 12. Furthermore, it is interesting to note that in the reaction of  $\text{CBr}_4$  with  $\text{CoW}^{7-}$  the charge change upon ET is  $-7 + 0 \rightarrow -6 + (-1)$ , while in the previous studies with heteropoly ions as oxidants toward alkylaromatics the changes were  $-5 + 0 \rightarrow -6 + 1$  and  $-7 + 0 \rightarrow -8 + 1$ . Thus, in the former case a repulsive electrostatic force and in the latter cases an attractive force develops upon ET. This will give quite large differences in the electrostatic correction term for  $\Delta G^{\circ'}$ , and could mean that if the added salts tend to alter the importance of this term, e.g., through ion pairing, one might possibly expect opposite behaviour for the heteropoly ions as oxidants and as reductants, respectively.

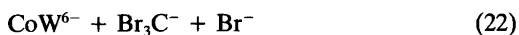
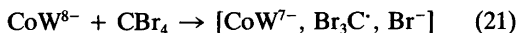
When  $[\text{Na}^+]$  or  $[\text{Me}_4\text{N}^+]$  was varied we found a saturation effect at around 0.1 M. This has previously been found for  $[\text{Bu}_4\text{N}^+]$ ,<sup>9a</sup> but in other studies  $k_{\text{ET}}$  has been found to vary linearly with both  $[\text{Na}^+]$  and  $[\text{K}^+]$  up to much higher concentrations.<sup>9a,24a</sup> If we use the points in the concentration range 1–10 mM we can extrapolate to a value for the rate constant at  $[\text{NaClO}_4] = 0$  mM of  $k_{\text{ET},[\text{Na}^+] = 0} = 1.06 \text{ M}^{-1} \text{ s}^{-1}$ . The concentrations of the remaining cations in the solution are then  $[\text{K}^+] = 1$  mM and  $[\text{TRISH}^+] = 1$  mM, and considering our own results, the effect of these should not be greater than to make it possible to ascertain that the rate constant for the retarded reaction would be very close to this value.

$\text{CoW}^{8-}$  is also expected to be an ET reagent.

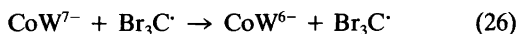
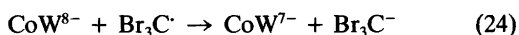
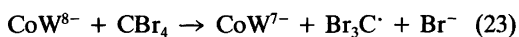
\* $\text{CHCl}_3$  has been described as a normal acid ( $\text{Brønsted } \alpha = 1$ ) with  $\text{p}K_a = 24$  in water.<sup>20</sup> Thus, its anion could be protonated by water in an almost diffusion-limited reaction. The difference in  $\text{p}K_a$  between  $\text{CHBr}_3$  and  $\text{CHCl}_3$  has been estimated to be quite small,  $\sim 2$   $\text{p}K_a$  units,<sup>21</sup> and taking into account the similarity of their respective anions we assume that the protonation of  $\text{Br}_3\text{C}^-$  also must be a very fast reaction.

<sup>8</sup>These values were calculated from the rate constants for the reaction of  $\text{CBr}_4$  with  $\text{CoW}^{7-}$ ,  $\text{Co(II)sep}^{2+}$ <sup>7</sup> and  $N,N,N',N'$ -tetramethyl-*p*-phenylenediamine (L. Ebersson and M. Ekström, to be published). They must be regarded as approximate, and we have only used them here to calculate relative reaction rates and our results are thus quite insensitive to changes in these values for  $\text{CBr}_4$ .

This prediction is borne out in the experiments since the rate increase in going from  $\text{CoW}^{7-}$  to  $\text{CoW}^{8-}$  is small (4 or 2, see below). If  $\text{CoW}^{8-}$  reacted by an ionic mechanism, one would expect a large increase in rate due to stabilizing bond formation in the transition state. Two reaction



*Scheme 2.*



*Scheme 3.*

schemes can be proposed (Schemes 2 and 3). In Scheme 2 it is supposed that the radical formed upon reduction of  $\text{CBr}_4$  never escapes the solvent cage but is immediately reduced to its anion by the second electron available. This would give second- or pseudo first-order kinetics with a rate law according to eqn. (27). If the tribromomethyl radical does escape from the cage we will arrive at the more complicated situation in Scheme 3.

$$\nu = k_{\text{ET}} [\text{CBr}_4][\text{CoW}^{7-}] \quad (27)$$

Here, we would expect some sort of biphasic behaviour as in the beginning of the reaction;  $[\text{CoW}^{8-}]$  will decrease and  $[\text{CoW}^{7-}]$  will increase. However, to obtain observable biphasic behaviour one should ideally have a large difference in rate constants for the successive steps and a difference in absorbance change for the two steps at the wavelength used.<sup>25</sup> The situation is rather the opposite in our case, and so even though the good first-order kinetics favour Scheme 2 we cannot entirely rule out Scheme 3.

Finally, with the previously mentioned estimates of  $E^\circ$  and  $\lambda$  for  $\text{CBr}_4$ ,  $E^\circ$  from Table 1,

$\lambda = 10 \text{ kcal mol}^{-1}$  and  $r_{12} = 9.5 \text{ \AA}$  for both  $\text{CoW}^{7-}$  and  $\text{CoW}^{8-}$ ,  $D = 51.3$  and  $\mu = 0.02 \text{ M}$ , Marcus' theory predicts the ratio  $k_{\text{ET},\text{CoW}^{8-}}/k_{\text{ET},\text{CoW}^{7-}}$  to be 3, in good agreement with our experimental results which, following Scheme 2, give the ratio as 4.

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