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### Rate of Reduction of Cobalt(III) Complexes by $\text{CO}_2^{\cdot-}$ Radicals in Aqueous Solution<sup>1</sup>

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Reduction of cationic cobalt(III) complexes by the hydrated electron,  $e_{\text{aq}}^-$ , is very fast with diffusion-controlled rates of  $(4-9) \times 10^{10} M^{-1} \text{sec}^{-1}$ .<sup>3</sup> Although the differences in these rates may be due to the charges and radii of the complexes,<sup>4</sup> the very low reduction potential of  $e_{\text{aq}}^-$  ( $E^\circ = -2.8 \text{ V}$ )<sup>3</sup> makes it an indiscriminant reagent and not kinetically selective. Recently, a great deal of interest has been directed toward the reactions of other radicals with Co(III) complexes in an attempt to aid in the elucidation of the mechanism of inter- and intramolecular electron transfer.<sup>5-8</sup> Of particular concern has been the correlation of the rate constant for the electron-transfer reaction of the radical with the complex with the potential of the redox couple and the free energy of the reaction and comparison with outer-sphere reactions involving metal ion reductants (e.g.,  $\text{Cr}^{2+}$ ,  $\text{Ru}(\text{NH}_3)_6^{2+}$ , and  $\text{V}^{2+}$ ).<sup>9,10</sup> We have chosen to examine the rate of reaction of  $\text{CO}_2^{\cdot-}$  radicals ( $E_{1/2}$  vs. sce =  $-1.3 \text{ V}$ )<sup>11</sup> with selected cobalt(III)-pentaammine and -tris-(bipyridyl) complexes to see if this milder reductant of 1-charge would show a greater selectivity in its reaction rates and reactivity patterns compared with those of  $e_{\text{aq}}^-$ .

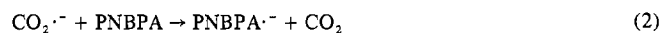
The technique of pulse radiolysis permits the  $\text{CO}_2^{\cdot-}$  radical to be generated conveniently in less than  $1 \mu\text{sec}$  via reaction 1 in solutions containing  $0.1 M \text{HCO}_2^-$  and  $2.5 \times 10^{-2} M$  OH or H +  $\text{HCO}_2^- \rightarrow \text{CO}_2^{\cdot-} + \text{H}_2\text{O}$  or  $\text{H}_2$

(1)

$$k_1 = 2.5 \times 10^9 \text{ or } 2.5 \times 10^8 M^{-1} \text{sec}^{-1}$$

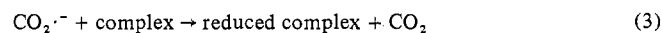
$\text{N}_2\text{O}$  (1 atm partial pressure in order to convert  $e_{\text{aq}}^-$  to  $\cdot\text{OH}$  radicals). However, because of the low absorptivity of the  $\text{CO}_2^{\cdot-}$  radical in accessible regions of the spectrum ( $\lambda_{\text{max}} 235 \text{ nm}$ ;  $\epsilon_{\text{max}} 3000 M^{-1} \text{cm}^{-1}$ ),<sup>12</sup> the disappearance of the radical cannot be conveniently observed. Similarly, most simple cobalt(III)-ammine complexes do not absorb appreciably above 280 nm thus restricting the possibility of monitoring the disappearance of the complex upon reduc-

tion by the radical. Furthermore, very few Co(III) complexes are known to give reduced intermediates which can be detected by absorption spectrophotometry. We have already reported<sup>6</sup> that *p*-nitrobenzoatopentaamminecobalt(III) ( $p\text{-O}_2\text{NC}_6\text{H}_4\text{CO}_2\text{Co}^{\text{III}}(\text{NH}_3)_5^{2+}$ ; PNBPA) reacts rapidly with  $\text{CO}_2^{\cdot-}$  to form a strongly absorbing transient intermediate ( $\lambda_{\text{max}} 330 \text{ nm}$ ;  $\epsilon_{\text{max}} 2.0 \times 10^4 M^{-1} \text{cm}^{-1}$ ).



$$k_2 = 1.9 \times 10^9 M^{-1} \text{sec}^{-1}$$

$\text{PNBPA}^{\cdot-}$  is relatively long-lived with its intramolecular decay to  $\text{Co}^{2+}$  having a rate constant  $2.6 \times 10^3 \text{ sec}^{-1}$ . From the competition for  $\text{CO}_2^{\cdot-}$  between PNBPA and the complex of interest, values of  $k_3$  can be evaluated.



### Experimental Section

$\text{N}_2\text{O}$ -saturated neutral solutions containing  $0.1 M \text{HCO}_2^-$  and  $4 \times 10^{-5} M$  PNBPA and up to  $2 \times 10^{-4} M$  of the complex of interest were subjected to 30-nsec pulses of 2.3-MeV electrons (dose/pulse  $\approx 1 \text{ krad}$ ) and the absorbance of  $\text{PNBPA}^{\cdot-}$  at 330 nm using a 2-cm optical path length was recorded.<sup>13</sup> Under the conditions of the experiments, the formation of  $\text{PNBPA}^{\cdot-}$  was complete within 40  $\mu\text{sec}$  after the pulse and showed very little decay ( $\sim 10\%$ ) during that time. The oscilloscopic traces, recorded on Polaroid film, were extrapolated back to "zero time" to give the absorbance of  $\text{PNBPA}^{\cdot-}$  under initial conditions. Solutions were prepared from triply distilled water that had been radiolyzed and photolyzed and were buffered using phosphate. The complexes were prepared using standard inorganic syntheses and were characterized by their absorption spectrum and elemental analysis.

### Results and Discussion

Competition for  $\text{CO}_2^{\cdot-}$  by a particular complex via reaction 3 causes a reduction in the amount of  $\text{PNBPA}^{\cdot-}$  generated in reaction 2. This is reflected by a diminution of the absorbance of  $\text{PNBPA}^{\cdot-}$  at 330 nm. At constant radiation dose per pulse, simple competition kinetics yields

$$k_3 = \frac{k_2[\text{PNBPA}]}{[\text{complex}]} \left( \frac{A^0 - A}{A} \right)$$

where  $A^0$  is the absorbance of  $\text{PNBPA}^{\cdot-}$  at 330 nm in the absence of added complex scavenger and  $A$  is the absorbance in the presence of complex. In the case of  $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{-CO}_2\text{Co}^{\text{III}}(\text{NH}_3)_5^{2+}$ ,  $k_3$  could be measured directly from the formation kinetics of the resulting transient at 295 nm (in the absence of PNBPA); for  $\text{Co}(\text{bipy})_3^{3+}$ ,  $k_3$  was obtained from the kinetics of the disappearance of the strong absorption of the complex at 330 nm (in the absence of PNBPA). In none of the other complexes was a reduced species detected; as well, the rate of electron transfer from  $\text{PNBPA}^{\cdot-}$  to the other complexes is too slow ( $k < 10^7 M^{-1} \text{sec}^{-1}$ ) to interfere with these measurements. Table I summarizes the data.

As expected, the  $\text{CO}_2^{\cdot-}$  radical is kinetically more selective than  $e_{\text{aq}}^-$  and the values of  $k(\text{CO}_2^{\cdot-} + \text{complex})$  show a range of over two orders of magnitude depending upon the nature of the ligands. The faster reactions shown by the aromatic nitro complexes are compatible with the strong electrophilic character of the nitro group;  $\text{CO}_2^{\cdot-}$  reacts rapidly ( $> 10^9 M^{-1} \text{sec}^{-1}$ ) with these free ligands. Thus, the coordination of these ligands does not remove the reactive site for  $\text{CO}_2^{\cdot-}$  attack and electron transfer. In the case of all the other complexes which show rate constants in the rather narrow range of  $10^7\text{-}10^8 M^{-1} \text{sec}^{-1}$ ,  $\text{CO}_2^{\cdot-}$  does not react with the

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**Table I.** Rate Constants for the Reaction of Co(III) Complexes with  $\text{CO}_2^{\cdot-}$  Radicals<sup>a</sup>

Complex	X	$k(\text{CO}_2^{\cdot-} + \text{complex}), M^{-1} \text{sec}^{-1}$
$\text{Co}(\text{NH}_3)_5\text{X}^{2+}$	$\text{NH}_3$	$1.1 (\pm 0.3) \times 10^8$
	$\text{H}_2\text{O}^b$	$1.7 (\pm 0.3) \times 10^8$
	$\text{OH}^-^c$	$< 3 (\pm 1.5) \times 10^7$
	$\text{Cl}^-$	$1.5 (\pm 0.3) \times 10^8$
	$\text{NO}_2^-$ (N bonded)	$< 2 (\pm 1) \times 10^7$
	$\text{NO}_3^-$ (O bonded)	$2.1 (\pm 0.3) \times 10^8$
	$\text{CH}_3\text{CO}_2^-$	$1.1 (\pm 0.3) \times 10^8$
	$\text{C}_6\text{H}_5\text{CO}_2^-$	$4.5 (\pm 2) \times 10^7$
	$\text{C}_6\text{H}_5\text{CH}_2\text{CO}_2^-$	$7.0 (\pm 2) \times 10^7$
	$\text{NC}_5\text{H}_4\text{CO}_2^-^d$ (O bonded)	$5.1 (\pm 2) \times 10^7$
	$\text{NC}_5\text{H}_5^e$ (N bonded)	$3.3 (\pm 0.4) \times 10^8$
	$p\text{-NCC}_6\text{H}_4\text{CO}_2^-$	$4.6 (\pm 2) \times 10^7$
	$p\text{-O}_2\text{NC}_6\text{H}_4\text{CO}_2^-$	$1.9 (\pm 0.1) \times 10^9$
	$p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{CO}_2^-$	$1.2 (\pm 0.1) \times 10^9$
$\text{Co}(\text{bipy})_3^{3+}$		$7.6 (\pm 0.1) \times 10^9$

<sup>a</sup> pH 6.9 unless otherwise indicated. <sup>b</sup> pH 5.2. <sup>c</sup> pH 7.8. <sup>d</sup> Pyridinecarboxylate. <sup>e</sup> Pyridine.

free ligands at a measurable rate ( $k < 10^7 M^{-1} \text{sec}^{-1}$ ). It should be noted, however, that although the  $\text{CO}_2^{\cdot-}$  radical does not react at a measurable rate with 2,2'-bipyridyl in neutral solution, it reacts rapidly with the protonated forms of the free ligand. Thus, the reactivity of the radical must be governed more by the nature of the complex as a whole than by the properties of the particular free ligand. But it is also clear that the small differences in the reduction potentials of the complexes, and thus the free energy changes of the reactions, do not correlate with the differences in the values of  $k$ .  $\text{Co}(\text{NH}_3)_6^{3+}$ , with  $E^\circ = 0.1 \text{ V}$ ,<sup>14</sup> exhibits a rate constant that is intermediate among the less reactive complexes and is about as reactive as  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$  with a reduction potential of 0.33 V.<sup>15</sup> No direct correlation can be seen among  $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$  ( $E^\circ \approx 0.3 \text{ V}$ ),<sup>16</sup>  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$  ( $E^\circ \approx 0.4$ ),<sup>16</sup> or the carboxylato complexes ( $E^\circ \approx 0.3 \text{ V}$ ).<sup>16</sup> A similar lack of correlation between the redox potential of the couple and the rate constant for reaction has been seen in the reaction of Co(III) complexes with  $\cdot\text{CH}_2\text{OH}$  radicals.<sup>8</sup> Similarly, there is no direct correlation between  $k(\text{CO}_2^{\cdot-} + \text{complex})$  and the overall charge on the complex.

The compounds examined appear to fall into two distinct categories: those that are highly reactive in which the reaction with  $\text{CO}_2^{\cdot-}$  involves the direct attack and electron transfer to an available orbital localized on the ligand and those that are only moderately reactive where the lower ligand orbitals are saturated and available antibonding orbitals are highly energetic. In the latter cases, the  $e_g^*$  orbitals of the metal center are at lower energy than any available ligand orbitals; the energy of the  $e_g^*$  orbital is affected by the nature of the X ligand, but again there does not appear to be any direct correlation with the position of the X ligand in the spectrochemical series.<sup>17</sup> However, the lower rate exhibited by these complexes could arise from radical attack at a face or edge of the octahedron which would be sterically restricted.

In the general sense, linear free energy correlations are certainly followed for  $e_{\text{aq}}^-$ ,  $\text{CO}_2^{\cdot-}$ , other radicals, and the milder chemical reducing agents with the highest reactivities

shown by the strongest reductants. The relative differences in the free energy change among the complexes when allowed to react with  $\text{CO}_2^{\cdot-}$  are small and so the differences in the rate constants are likewise expected to be small. That there is no apparent correlation between the redox potential and the rate constant no doubt arises from other factors that contribute to the reactivity when the differences in the free energy changes are small.

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**Registry No.**  $\text{CO}_2^{\cdot-}$ , 14485-07-5;  $\text{Co}(\text{NH}_3)_6^{2+}$ , 14695-95-5;  $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ , 14403-82-8;  $\text{Co}(\text{NH}_3)_5\text{OH}^+$ , 16632-75-0;  $\text{Co}(\text{NH}_3)_5\text{Cl}^+$ , 14970-14-0;  $\text{Co}(\text{NH}_3)_5\text{NO}_2^+$ , 16633-04-8;  $\text{Co}(\text{NH}_3)_5\text{NO}_3^+$ , 15077-47-1;  $\text{Co}(\text{NH}_3)_5(\text{CH}_3\text{CO}_2)^+$ , 16632-78-3;  $\text{Co}(\text{NH}_3)_5(\text{C}_6\text{H}_5\text{CO}_2)^+$ , 30931-77-2;  $\text{Co}(\text{NH}_3)_5(\text{C}_6\text{H}_5\text{CH}_2\text{CO}_2)^+$ , 40544-43-2;  $\text{Co}(\text{NH}_3)_5(\text{NC}_5\text{H}_4\text{CO}_2)^+$ , 40544-44-3;  $\text{Co}(\text{NH}_3)_5(\text{NC}_5\text{H}_5)^+$ , 31011-67-3;  $\text{Co}(\text{NH}_3)_5(p\text{-NCC}_6\text{H}_4\text{CO}_2)^+$ , 40544-46-5;  $\text{Co}(\text{NH}_3)_5(p\text{-O}_2\text{NC}_6\text{H}_4\text{CO}_2)^+$ , 36445-08-6;  $\text{Co}(\text{NH}_3)_5(p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{CO}_2)^+$ , 40544-48-7;  $\text{Co}(\text{bipy})_3^{3+}$ , 19052-39-2.

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### Tris(dichloroboryl)methane, Bis(dichloroboryl)methane, and a Possible New Route to Carboranes<sup>1</sup>

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The availability of tetrakis(dimethoxyboryl)methane and related compounds<sup>2</sup> suggested to us the possibility of a new route to the smaller carboranes. However, our attempts at direct reduction failed,<sup>2,3</sup> and a good synthesis of carboranes from acetylene and pentaborane has been reported recently.<sup>4</sup> There remains some possible advantage in reducing the boron at a later stage of the synthesis and also the possibility of synthesizing new *nido*-carboranes, and we have explored the preparation and reduction of bis- and tris(dichloroboryl)-methane with this objective in mind.

The rationale for using the chloro compounds was that their reduction should be easier than that of the alkoxy derivatives tried earlier, which undergo loss of boron and polymerization on treatment with basic reducing agents.<sup>2</sup> We began by trying to make tetrakis(dichloroboryl)methane,  $\text{C}(\text{BCl}_2)_4$ , from tetrakis(dimethoxyboryl)methane,  $\text{C}[\text{B}(\text{OCH}_3)_2]_4$ , and boron trichloride or other reactive chlorides but obtained only polymeric products,<sup>3</sup> even though  $\text{C}(\text{BCl}_2)_4$  has been prepared in small quantities from carbon vapor and  $\text{B}_2\text{Cl}_4$  and is stable when pure.<sup>5</sup> Tris(dichloroboryl)methane seemed more promising, inasmuch as Castle

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