Pulse Radiolysis Study of the Reactions of Some Reduced Metal Ions with Molecular Oxygen in Aqueous Solution

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Abstract: A pulse radiolysis study of the product of the reaction of zerovalent mercury and silver, monovalent cadmium, cobalt, copper, nickel, lead, and zinc, and divalent chromium with molecular oxygen has been made. With Ag, Hg, Cd, Co, Pb, and Zn the product transferred an electron to benzoquinone and is identified as O_2^-, or some complex of the reduced metal with O_2, which has properties similar to those of O_2^-. With Ni and Cr no electron transfer occurred, and the product is suggested to be a complex, NiO_2^+ and CrO_2^{2+}, respectively. These have characteristic absorption spectra (NiO_2^+ λ_{max} 265 nm, ϵ_{max} 2700 $M^{-1}\ cm^{-1}$; CrO_2^{2+} λ_{max} 245 and 290 nm, ϵ_{max} 7800 and 3200 $M^{-1}\ cm^{-1}$, respectively). CrO_2^{2+} is long-lived under the conditions employed ($[Cr^{2+}] \ll [O_2]$). Studies on the reactivity of NiO_2^+ with tetranitromethane reveal (i) that the complex protonates ($pK = 3.2 \pm 0.3$) and (ii) that both protonated and unprotonated complexes decay by a unimolecular reaction to give O_2^- and HO_2, respectively. With Cu no electron transfer to benzoquinone was detected, but was found with tetranitromethane, and it is suggested that the reaction $Cu^+ + O_2$ is too slow to be studied by this method, or that the reaction is an equilibrium which lies strongly in favor of the reactants under the conditions of the experiments described.

The lower valency states of many metal ions and their complexes are oxidized by molecular oxygen.[2] The initial reaction may involve electron transfer to give the superoxide radical anion (1a) or coordination of the O_2 to form a complex (1b). Many examples are known[2,3] where reaction 1b occurs

$$M^{n+} + O_2 \begin{array}{l} \nearrow\ M^{(n+1)+} + O_2^- \qquad (1a) \\ \searrow\ MO_2^{n+} \qquad\qquad\quad (1b) \end{array}$$

reversibly, and this pathway is of considerable importance in some biological oxidations.[4] We report here a pulse radiolysis study of the products of the reaction of zerovalent mercury and silver, monovalent cadmium, cobalt, copper, lead, nickel, and zinc, and divalent chromium with molecular oxygen. To distinguish between the pathways represented by 1a and 1b we have measured the reactivity of the product (designated P) with benzoquinone and tetranitromethane, both of which are rapid scavengers of O_2^-. With Cr and Ni, P has also been characterized by direct observation. Some preliminary results on the $Cr^{2+} + O_2$ reaction have been described in an earlier publication.[5]

Experimental Section

Materials. All solutions were prepared from triply distilled water, and their pH was adjusted with sodium hydroxide or perchloric acid. Lead was used as the acetate, mercury as the chloride, and the other metal ions as their sulfate salts. All were of analytical reagent grade. 1,4-Benzoquinone was purified by sublimation at least twice before use, and tetranitromethane by repeated washings with water. Solutions of tetranitromethane were prepared by dilution of saturated tetranitromethane solutions, and the concentrations calculated assuming a maximum solubility of 6.4×10^{-3} M at 25 °C.

Apparatus and Procedure. Pulse radiolysis experiments were carried out using 0.5–5.0 μs pulses of 1.6 MeV electrons from a Van de Graaff accelerator. The optical system consisted of a 450-W xenon lamp, a 1.5 cm path length cell, a Zeiss MQ4 III prism monochromator, and an EMI 9558 QB photomultiplier. Conductivity measurements were made with the ac cell described by Kelm et al.[6] Other details of the apparatus have been given elsewhere.[7]

Rate constants were evaluated from plots of log (optical density) against time, which in all cases were linear over at least three half-lives. For each particular set of conditions the rate constant values quoted are the mean of four or five separate determinations. Dosimetry was performed using aerated 10^{-2} M CNS^- solutions, and taking $G((CNS)_2^-) = 2.8$ and $\epsilon_{475}((CNS)_2^-) = 7600\ M^{-1}\ cm^{-1}$. All measurementwere made at 25 ± 2 °C.

Results and Discussion

Electron Transfer to 1,4-Benzoquinone. Benzoquinone reacts rapidly with O_2^- (reaction 2, $k = 9.8 \times 10^8\ M^{-1}\ s^{-1}$ [8]) to form

$$O_2^- + C_6H_4O_2 \longrightarrow O_2 + C_6H_4O_2^- \qquad (2)$$

the benzosemiquinone radical anion, $C_6H_4O_2^-$ (λ_{max} 430 nm, ϵ_{max} 7250 $M^{-1}\ cm^{-1}$, $pK_a = 4.0$[9]). In acid solutions, where the superoxide radical exists in its protonated form, HO_2 ($pK_a = 4.88$[10]), electron transfer to benzoquinone is much slower ($k \leq 10^7\ M^{-1}\ s^{-1}$ [11]).

Experiments on the reactivity of the product, P, with benzoquinone were performed by pulse radiolysis of solutions containing (5–200) $\times 10^{-3}$ M of the metal ion, 1 M *tert*-butyl alcohol, 1.3×10^{-3} M O_2 and (2–4) $\times 10^{-5}$ M benzoquinone. These conditions ensured almost quantitative (>90%) formation of P within a few microseconds via reactions 3–5.

$$H_2O \longrightarrow e_{aq}^-,\ H,\ OH,\ H_2,\ H_2O_2,\ H^+ \qquad (3)$$

$$e_{aq}^- + M^{n+} \longrightarrow M^{(n-1)+} \qquad (4)$$

$$M^{(n-1)+} + O_2 \longrightarrow P \qquad (5)$$

$$M^{(n-1)+} + C_6H_4O_2 \longrightarrow M^{n+} + C_6H_4O_2^- \qquad (6)$$

In addition the rate of reaction of the reduced metal ion, $M^{(n-1)+}$, with benzoquinone (eq 6) was determined by pulse radiolyzing similar deaerated solutions. *tert*-Butyl alcohol was added to scavenge the hydroxyl radicals, and convert them into $CH_2(CH_3)_2COH$ radicals (deaerated solutions) or the corresponding peroxy radical (oxygenated solutions). These are weakly absorbing and relatively inert species, and in general produce no mechanistic complications. The rate constants for the reactions of P and $M^{(n-1)+}$ with benzoquinone were measured by monitoring the rate of formation of benzosemiquinone at 430 nm. The values found are shown in Table I.

The reaction of $M^{(n-1)+}$ with benzoquinone is rapid (except Cu^+), and the rate constants are appreciably different from those for $P + C_6H_4O_2$. The values of k_6 for $M^{(n-1)+} = Cd^+$, Co^+, and Zn^+ are close to those reported by Rao and Hayon,[18] but that for $M^{(n-1)+} = Cr^{2+}$ is approximately a factor of ten less. The product, P, reacts with benzoquinone at a rate very similar to that of O_2^- when $M^{(n-1)+} = Ag_3^+$, Cd^+, Co^+, HgCl, Pb^+, and Zn^+. We conclude therefore that P for these metal ions is either O_2^- itself, some complex between the metal ion and O_2 (e.g., an outer sphere complex) which behaves like O_2^-, or that a complex exists which breaks down rapidly ($\tau_{1/2}$

Table I. Kinetic Data for Electron Transfer to Benzoquinone

M^{n+}	$[M^{n+}]$ $10^3 M$	$M^{(n-1)+}$	$M^{(n-1)+} + O_2 \rightarrow P$ $k/M^{-1}\,s^{-1}$	Ref	$M^{(n-1)+} + C_6H_4O_2$[a] $k/M^{-1}\,s^{-1}$	$P + C_6H_4O_2$[a] $k/M^{-1}\,s^{-1}$	pH
Ag^+	5	$Ag_3{}^{+}$[b]	3.8×10^8	*c*	1.5×10^8	7.3×10^8	5.8
Cd^{2+}	10	Cd^+	3.0×10^9	14–16	4.1×10^9	7.5×10^8	5.4
Co^{2+}	100	Co^+	6.0×10^9	16	5.1×10^9	5.4×10^8	4.7
Cr^{3+}	10	Cr^{2+}	1.6×10^8	This work	3.2×10^8	$\leqslant 5 \times 10^7$	4.8
Cu^{2+}	10	Cu^+	?	—	$\leqslant 10^6$	$\leqslant 5 \times 10^7$	4.9
$HgCl_2$	6	$HgCl$[d]	1.0×10^9	17	3.9×10^9	1.1×10^9	5.1
Ni^{2+}	10	Ni^+	1.8×10^9	14, 15	2.3×10^8	$\leqslant 5 \times 10^7$	6.0
Pb^{2+}	10	Pb^+	3.9×10^9	14	4.1×10^9	6.2×10^8	6.3
Zn^{2+}	200	Zn^+	2.8×10^9	14, 15	3.0×10^9	5.6×10^8	5.7
None[e]	—	—	—	—	—	7.8×10^8	6.9

[a] Measured from the rate of formation of benzosemiquinone at 430 nm. Uncertainty ±20%, $T = 25 \pm 2$ °C, pH given in final column. Solutions subject to doses of ca. 0.5 krad/pulse. [b] See ref 12. [c] Reinterpreted from data in ref 13 assuming mechanism for Ag^+ reduction quoted in ref 12. [d] See ref 17. [e] Solutions contained 5×10^{-2} M $HCO_2{}^-$; $P \equiv O_2{}^-$.

$\lesssim 10\ \mu s$) to give $O_2{}^-$ (eq 7a) or is in equilibrium with $O_2{}^-$ (eq 7b).

$$MO_2{}^{(n-1)+} \nearrow M^{n+} + O_2{}^- \qquad (7a)$$

$$MO_2{}^{(n-1)+} \rightleftharpoons M^{n+} + O_2{}^- \qquad (7b)$$

The absorption spectra and decay kinetics of P for the metal ions Cd^+, Co^+, and Zn^+ have been reported.[16] The data were not dissimilar from those expected if P is $O_2{}^-$, but the formation of metal complexes could not be ruled out.

With Cr, Cu, and Ni no transfer to benzoquinone was found in oxygenated solutions, and it follows that *no* $O_2{}^-$ is formed under the conditions employed. These three metal ions were selected for further study.

$Cr^{2+} + O_2$. The experiments described above with chromium were confirmed using tetranitromethane. Like benzoquinone this is reactive with $O_2{}^-$ ($k = 2.0 \times 10^9\ M^{-1}\,s^{-1}$ [19,20]) (eq 8), but not with HO_2 ($k < 1.9 \times 10^5\ M^{-1}\,s^{-1}$ [20]), and gives rise to the nitroform anion (λ_{max} 350 nm, ϵ_{max} 14 600 $M^{-1}\,cm^{-1}$ [20]).

$$O_2{}^- + C(NO_2)_4 \longrightarrow O_2 + C(NO_2)_3{}^- + NO_2 \qquad (8)$$

In deaerated solutions, where reaction 9 occurs, an exponential formation of the nitroform anion was observed at 350 nm with $G[C(NO_2)_3{}^-] = 2.6$. The pseudo-first-order rate

$$Cr^{2+} + C(NO_2)_4 \longrightarrow Cr^{3+} + C(NO_2)_3{}^- + NO_2 \qquad (9)$$

constant for the reaction was linearly dependent on $[C(NO_2)_4]$ (3.18–18.6×10^{-5} M)[21] giving $k_9 = (1.2 \pm 0.2) \times 10^8\ M^{-1}\,s^{-1}$. When the solutions were saturated with oxygen $G[C(NO_2)_3{}^-]$ was reduced to 0.9. This can be identified with a small yield of $O_2{}^-$ originating from (i) reaction of the radiolytically produced H atoms ($G = 0.6$) with oxygen (eq 10), and (ii) small fraction of the hydrated electrons scavenged directly by the O_2 ($G = 0.2$).

$$H + O_2 \longrightarrow HO_2 \rightleftharpoons H^+ + O_2{}^- \qquad (10)$$

The pulse radiolysis of aerated aqueous solutions containing only 10^{-2} M Cr^{3+} + 0.5 M *tert*-butyl alcohol produced the spectra shown in Figure 1. Following the pulse there was a first-order buildup of absorption, and then a much slower decay to a plateau. Under these conditions the hydrated electrons are converted by reaction with Cr^{3+} to Cr^{2+}, which reacts in turn with O_2; the OH radicals give the *tert*-butyl alcohol peroxy radical (see above), and the H atoms give HO_2 via reaction 10. The spectrum measured at 50 μs is attributed to the product of the reaction $Cr^{2+} + O_2$, with minor contributions from the *tert*-butyl alcohol peroxy radical and HO_2. The product is clearly not $O_2{}^-$ (λ_{max} 240 nm, ϵ_{max} 2000 $M^{-1}\,cm^{-1}$ [10]), the species that would result if the reaction involved electron transfer. This finding is in accord with the transfer experiments described above, and we shall write the product as $CrO_2{}^{2+}$.

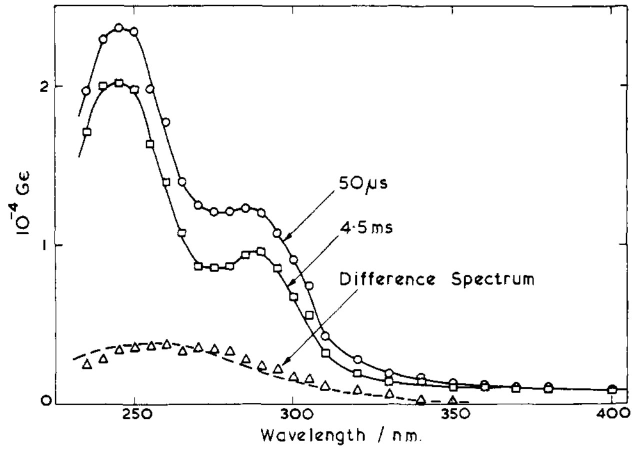

Figure 1. Spectra of the transients produced by the pulse radiolysis of aerated solutions of 10^{-2} M Cr^{3+} + 0.5 M *tert*-butyl alcohol, pH 3.4, dose ca. 500 rad pulse^{-1}: (○) measured 50 μs after the pulse; (□) 4.5 ms after the pulse (spectrum of $CrO_2{}^{2+}$); (△) difference spectrum, and (- - -) spectrum of the *tert*-butyl alcohol peroxy radical from ref 24 taking G = 2.8.

Table II. Kinetic Data for the Reaction $Cr^{2+} + O_2$[a]

$10^3[Cr^{3+}]/M$	$10^4[O_2]/M$	pH	$10^{-4}k_{obsd}{}^{b}/s^{-1}$
2	2.6	3.3	4
2	2.6	4.3	4
10	2.6	3.4	4
10	13	2.6	21
10	13	3.4	21
10	13	3.8	20

[a] All solutions contained also 0.5 M *tert*-butyl alcohol. Dose ca. 500 rad pulse^{-1}, I = 0.1 M. [b] Rate constants measured from the rate of formation of product at 300 nm. Uncertainty ±10%.

The buildup was first order in $[O_2]$ and independent of pH and $[Cr^{3+}]$ (see Table II). We attribute this to reaction 11, and estimate $k_{11} = (1.6 \pm 0.2) \times 10^8\ M^{-1}\,s^{-1}$. The value of k_{11} was also measured by competition with benzoquinone. The reactions involved are:

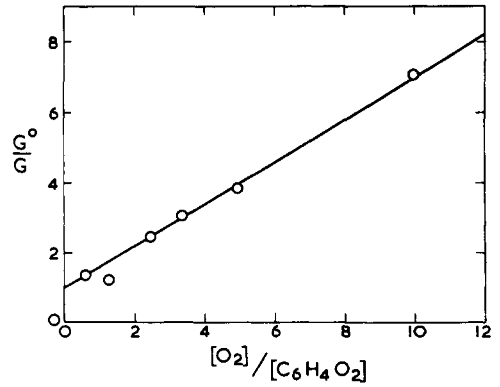

Figure 2. Competition for Cr^{2+} between O_2 and benzoquinone. G is the yield of the benzosemiquinone radical at 410 nm; G^0 taken as 2.8. Solutions contained also 10^{-2} M Cr^{3+} + 0.5 M *tert*-butyl alcohol, pH 3.1; dose ca. 700 rad pulse^{-1}.

$$Cr^{2+} + O_2 \longrightarrow CrO_2^{2+} \qquad (11)$$

$$Cr^{2+} + C_6H_4O_2 \longrightarrow Cr^{3+} + C_6H_4O_2^- \qquad (12)$$

It has been shown above that CrO_2^{2+} is unreactive with benzoquinone (Table I), and so the system is free of complicating side reactions. A good competition plot was obtained (see Figure 2), the slope of which gives $k_{11}/k_{12} = 0.60$. Independent experiments in deaerated solutions[22] give $k_{12} = (3.2 \pm 0.3) \times 10^8$ M^{-1} s^{-1}, and hence $k_{11} = (1.9 \pm 0.3) \times 10^8$ M^{-1} s^{-1}, in good agreement with the value from the direct determination.

Experiments were also performed using the ac conductivity technique to see whether reaction 11 is accompanied by uptake or loss of protons. With increasing pH (3.3-4.3) a decrease in the end of pulse conductivity was found. This is attributable to the effect of hydrolysis of Cr^{3+} (eq 13) on the reaction of Cr^{III} with e_{aq}^-. At the lower pH's reaction 14 predominates, and the observed signal is due principally to the radiation produced H^+ (reaction 3). At higher pH's reaction 15 becomes important, the OH^- produced neutralizes the radiolytic H^+ within the pulse, and only a small conductivity signal is detected. At no pH was any post-pulse change in conductivity found, and hence the reaction $Cr^{2+} + O_2$ is not accompanied by loss or uptake of protons.

$$CrOH_2^{3+} \rightleftharpoons CrOH^{2+} + H^+ \qquad (13)$$

$$e_{aq}^- + Cr^{3+} \longrightarrow Cr^{2+} \qquad (14)$$

$$e_{aq}^- + CrOH^{2+} \longrightarrow Cr^{2+} + OH^- \qquad (15)$$

The decay noted at long times in the optical experiments is probably due to the disappearance of the *tert*-butyl alcohol peroxy radicals (and possibly HO_2[23]). In support of this it was found that the difference of the spectra at 50 μs (aerated solutions) and of the plateau at 4.5 ms was of the same shape and magnitude (taking $G = 2.8$) as an authentic *tert*-butyl alcohol peroxy radical spectrum.[24] The spectrum at 4.5 ms is then due almost entirely to CrO_2^{2+}, which has therefore λ_{max} 245 and 290 nm, ϵ_{max} 7800 ± 800 and 3200 ± 300 M^{-1} cm^{-1}, respectively, assuming that it is formed with a yield of $G = 2.8$.[23] No evidence for the decay of CrO_2^{2+} was found. Indeed a permanent drop in the photomultiplier current was observed in these solutions at wavelengths near 260 nm, where CrO_2^{2+} absorbs intensely, and it seems that this or some species subsequently formed is quite long-lived under the conditions of our experiments.

We have no evidence for the reversibility of reaction 11 but cannot rule out this possibility. The benzoquinone transfer experiments indicate that the equilibrium, if it exists, lies well to the right, and we estimate $K_{11} \geq 2 \times 10^5$ M^{-1}. A recent report suggests that the reaction may be reversible, for it has been observed that anhydrous chromium(II) ion exchanged A type zeolite reversibly binds O_2.[25]

Chromium(II) is known to be oxidized by O_2 with the stoichiometry given by eq 16 when $[Cr^{2+}] \gg [O_2]$.[26] The ultimate

$$4Cr^{II} + O_2 + 4H^+ = 4Cr^{III} + 2H_2O \qquad (16)$$

product of the reaction under these conditions has been shown to be $Cr(OH)_2Cr^{4+}$ by ^{18}O exchange studies,[26] its charge,[27] and the fact that the same species is produced when Cr^{3+} solutions are heated.[28] The mechanism of its formation was postulated to involve a peroxy bridged intermediate, CrO_2Cr^{4+}, since both of the oxygen atoms from O_2 are incorporated into the product without exchange with the solvent.[26] No long-lived intermediate such as CrO_2^{2+} was detected. This is probably becausthe lifetime of CrO_2^{2+} is considerably reduced when $[Cr^{2+}] \gg [O_2]$, through the occurrence of reaction 17. Formation of the ultimate product,

$$CrO_2^{2+} + Cr^{2+} \longrightarrow CrO_2Cr^{4+} \qquad (17)$$

$Cr(OH)_2Cr^{4+}$, then presumably occurs through further reduction by two more equivalents of Cr^{2+} and protonation. It is probably these reactions that give rise to the rate equation (eq 18) determined for this system by Kolaczkowski and Plane.[26,29]

$$-d[Cr^{2+}]/dt = k[Cr^{2+}]^2 \qquad (18)$$

When $[O_2] \gg [Cr^{2+}]$ there is evidence that oxidation to chromic acid occurs.[30] The stoichiometry of the reaction is unknown, but it is clear that CrO_2^{2+} is produced as the initial intermediate. These solutions can oxidize alcohols to aldehydes, arsenite to arsenate, iodide to iodine, etc.,[30,31] and in the latter case Piccard[30] has found evidence for at least three intermediate chromium-oxygen species. It is also of interest to note that in ammoniacal solutions the formation of the peroxy complex $(H_3N)_5CrO_2^{2+}$ has been postulated,[32] and that at low Cr^{II} concentrations this is thought to be oxidized by water to Cr^{IV} and H_2O_2.

$Cu^+ + O_2$. The lack of formation of benzosemiquinone in both oxygenated and deaerated solutions of copper and uncertainty about the value of $k(Cu^+ + O_2)$ prevent any definite statement about the nature of the product, P, in this case. The experiments were therefore repeated using tetranitromethane, which is known to be reactive with Cu^+.[19]

In deaerated solutions containing 10^{-2} M Cu^{2+}, 0.5 M *tert*-butyl alcohol, and 4.2×10^{-5} M tetranitromethane (pH 4.6) the formation of the nitroform anion consisted of two parts: a rapid reaction with $\tau_{1/2}$ = ca. 30 μs, and a slower step with $\tau_{1/2}$ = ca. 500 μs. This experiment was repeated (i) in the absence of *tert*-butyl alcohol (the hydroxyl radicals are now scavenged by Cu^{2+}) when only the rapid process was observed, and (ii) in N_2O saturated solutions containing *tert*-butyl alcohol, when only the slow process was observed. The results are summarized in Table III. The rapid process shows a linear dependence on $[C(NO_2)_4]$ and is attributed to reaction 19. From the data in Table III (deaerated solutions) a value of $k_{19} = (4.7 \pm 0.5) \times 10^8$ M^{-1} s^{-1} is found, which is in good agreement with the rate constant $k_{19} = (4.2 \pm 0.4) \times 10^8$ M^{-1} s^{-1} reported by Asmus et al.[19]

$$Cu^+ + C(NO_2)_4 \longrightarrow Cu^{2+} + C(NO_2)_3^- + NO_2 \qquad (19)$$

The slow process showed no dependence on $[C(NO_2)_4]$, [*tert*-butyl alcohol], or pH in the ranges studied, and only a

Table III. Kinetic Data from the Cu^{2+}/Tetranitromethane System

$10^3[Cu^{2+}]$/M	[*tert*-butyl alcohol]/M	$10^6[C(NO_2)_4]$/M	pH	$10^{-3}k_{obsd}{}^{a}$/s^{-1}
		Deaerated Solutions		
5	0	31.8	4.9	15
5	0	63.4	4.9	29
5	0	125.5	4.9	60
		N_2O Saturated Solutions		
0.1	0.5	31.8	5.9	0.73
0.5	0.5	31.8	5.3	1.3
1.0	0.5	31.8	4.8	1.5
2.0	0.5	31.8	4.9	1.5
5.0	0.5	31.8	4.9	1.7
1.0	0.5	63.4	5.1	1.4
1.0	0.5	125.5	5.2	1.8
1.0	0.1	31.8	5.2	1.5
1.0	0.5	31.8	3.3	1.3
		O_2 Saturated Solutions		
10	0.5	21.2	4.6	12
10	0.5	21.2	3.4	12

[a] Rate constants measured from the rate of formation of the nitroform anion at 350 nm. Uncertainty ±10%, dose ca. 300 rad $pulse^{-1}$; various ionic strengths.

slight dependence on $[Cu^{2+}]$. The yield of the nitroform anion, however, showed a marked dependence on $[Cu^{2+}]$. In this system the hydrated electrons and hydroxyl radicals are converted into $CH_2(CH_3)_2COH$ radicals by reactions 20 and 21.

$$e_{aq}^- + N_2O \xrightarrow{H_2O} N_2 + OH + OH^- \tag{20}$$

$$OH + (CH_3)_3COH \longrightarrow H_2O + CH_2(CH_3)_2COH \tag{21}$$

The reaction of the $CH_2(CH_3)_2COH$ radical with tetranitromethane is known to be slow,[33] and hence the nitroform anion must form via reduction of Cu^{2+} by $CH_2(CH_3)_2COH$ and reaction 18. In view of the independence of the rate of formation of the nitroform anion on both $[C(NO_2)_4]$ and $[Cu^{2+}]$, we tentatively suggest that an intermediate, possibly a radical-Cu^{II} complex, is formed and that the unimolecular breakdown of this is the rate determining step. The variation of the yield of the nitroform anion on $[Cu^{2+}]$ indicates that other reactions occur which involve consumption of the reacting species.

In oxygenated Cu^{2+} solutions with *tert*-butyl alcohol present the nitroform anion was formed in a rapid single step which was independent of pH (Table III). These results suggest (i) that the $CH_2(CH_3)_2COH$ radicals are scavenged predominantly by O_2, and (ii) that no O_2^- is formed. Indeed the similarity of the rate constants with those formed in the deaerated solutions provides strong circumstantial evidence that the species reacting with tetranitromethane is Cu^+. Assuming this to be the case it can be concluded that under the conditions of these experiments either reaction 22 is too slow to compete with eq 19, and therefore $k_{22} \leq$ ca. 10^6 M^{-1} s^{-1}, or that eq 22 is reversible, the reverse reaction being much more rapid than the forward reaction.

$$Cu^+ + O_2 \longrightarrow \text{products} \tag{22}$$

It is well known that Cu^+ is oxidized by O_2, and that the reaction ultimately yields H_2O_2.[34] With Cu^I chloride complexes the rate constant for the oxidation is ca. 250 M^{-1} s^{-1},[35] and for bipyridyl Cu^I ions is 6.5×10^3 M^{-1} s^{-1}.[36] A value of k_{22} = ca. 10^6 M^{-1} s^{-1} has been estimated by Zuberbühler[37] from experiments on the oxidation of $Cu(CH_3CN)_2^+$ by O_2, but some doubt is attached to this figure.[38] Reversible addition of O_2 has been found with all complexes studied,[35-37,40] and where information is available the equilibrium favors the complex.[36]

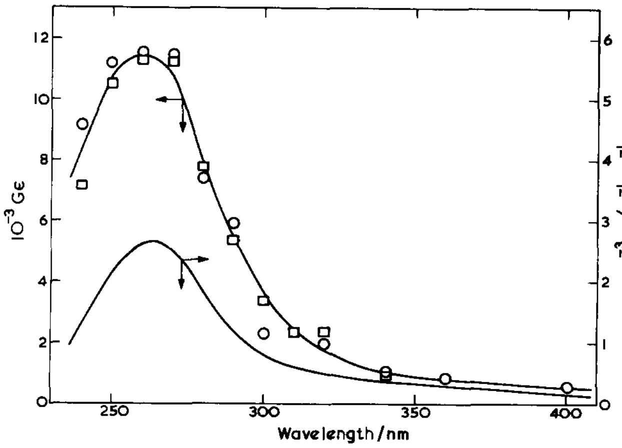

Figure 3. Spectra of transients produced by the pulse radiolysis of oxygenated solutions of 10^{-2} M Ni^{2+} + 0.5 M *tert*-butyl alcohol at pH 3.6 (□) and 6.2 (○). Lower curve is the spectrum of NiO_2^+ obtained by correction of the measured spectra for absorption by the *tert*-butyl alcohol peroxy radical and HO_2/O_2^-, taking $G(NiO_2^+)$ = 2.55.

Table IV. Kinetic Data on the Formation of the Nitroform Anion Following the Reaction $Ni^+ + O_2{}^{a}$

$10^3[Ni^{2+}]$/M	$10^4[O_2]$/M	$10^6[C(NO_2)_4]$/M	pH	$10^{-2}k_{obsd}$/s^{-1}
10	0	31.8	5.92	430
10	0	63.4	5.90	900
10	0	125.5	5.90	1800
10	0	186.4	5.85	2500
10	13	63.4	5.67	7.7
10	13	63.4	5.15	8.1
5	13	63.4	5.05	9.1
10	13	31.8	5.05	7.7
10	13	63.4	5.00	8.5
10	13	125.5	5.00	8.8
10	2.6	63.4	5.07	8.5
100	13	63.4	5.07	7.4
10	13	63.4	4.45	9.5
10	13	63.4	4.13	10.2
10	13	63.4	3.70	14
10	13	63.4	3.37	21
10	13	63.4	3.20	23
10	13	63.4	3.05	23
10	2.6	63.4	3.05	23
10	13	31.8	3.05	14
10	13	125.5	3.05	26
100	13	63.4	3.05	22

[a] All solutions contained also 1 M *tert*-butyl alcohol. Dose ca. 200 rad $pulse^{-1}$; I = 0.04 M except in solutions containing 0.1 M Ni^{2+}.

$Ni^+ + O_2$. It has previously been shown[16] that the product of the reaction $Ni^+ + O_2$ absorbs more intensely than does O_2^-, although of similar shape and peak position. The spectrum reported was measured in the presence of formate ion, and so contained a relatively large contribution from O_2^- produced via the reaction $CO_2^- + O_2$. We have remeasured the spectrum in the presence of 0.5 M *tert*-butyl alcohol as an OH scavenger at pH's 3.6 and 6.2 (see Figure 3). The *tert*-butyl alcohol peroxy radicals (G = 2.8) and HO_2/O_2^- (G = 0.85) also present make minor contributions to the absorption, and when the spectrum is corrected for these the product of $Ni^+ + O_2$ is found to have λ_{max} 265 nm, ϵ_{max} 2700 ± 500 M^{-1}

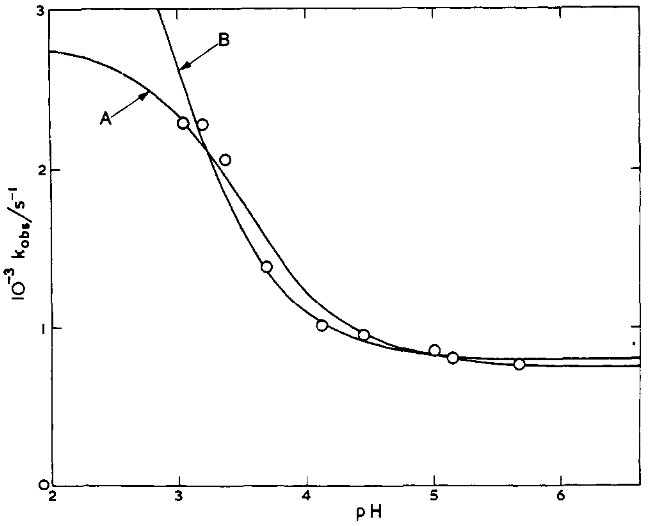

Figure 4. Effect of pH on the observed rate constant, k_{obsd}, for the formation of the nitroform anion in oxygenated solutions containing 10^{-2} M Ni^{2+}, 1 M *tert*-butyl alcohol, and 6.3×10^{-5} M tetranitromethane. Lines calculated from eq 24 taking $k_a = 750\ s^{-1}$, $k_b = 2800\ s^{-1}$, $K = 3200\ M^{-1}$ for curve A, and $k_a = 800\ s^{-1}$, $k_b = 5000\ s^{-1}$, $K = 770\ M^{-1}$ for curve B.

cm^{-1}, independent of pH, assuming it is formed with $G = 2.55$ (0.25 e_{aq}^- react with the O_2). This absorption has been attributed[16] to the formation of a complex, written as NiO_2^+, by reaction 23. The benzoquinone experiments described above are in accord with this.

$$Ni^+ + O_2 \longrightarrow NiO_2^+ \tag{23}$$

When tetranitromethane was used in place of benzoquinone a slow first-order formation of the nitroform anion occurred. This was independent of $[Ni^{2+}]$, $[O_2]$, and $[C(NO_2)_4]$ (at pH 5.1), slightly dependent on $[C(NO_2)_4]$ at pH 3.05, and increased with decreasing pH. The rate constants measured and the conditions employed are shown in Table IV. We interpret the results according to the scheme shown below where the

$$\begin{tikzcd}
NiO_2^+ + H^+ \arrow[r, leftrightharpoons, "K"] \arrow[d, "k_a"] & NiO_2H^{2+} \arrow[d, "k_b"] \\
(Ni^{2+} +)\ O_2^- + H^+ \arrow[r, leftrightharpoons, "pK=4.88"] \arrow[d, "C(NO_2)_4"] & HO_2\ (+ Ni^{2+}) \\
C(NO_2)_3^-\ (+ NO_2 + O_2) &
\end{tikzcd}$$

processes represented by the rate constants k_a and k_b are rate determining. The observed rate constant, k_{obsd}, for the formation of the nitroform anion will therefore be given by:

$$k_{obsd} = \frac{k_a + k_b K[H^+]}{1 + K[H^+]} \tag{24}$$

The dependence of k_{obsd} on pH is shown in Figure 4. The curves, which represent two extreme cases, have been calculated using eq 24 and the values of k_a, k_b, and K indicated. No attempt to find the best curve through the points has been made because of the large uncertainties in the experimental data. Approximate values of the constants are $k_a = 780 \pm 80\ s^{-1}$, $k_b \geqslant 2800\ s^{-1}$, and $K = 2000 \pm 1200\ M^{-1}$ (i.e., the acid dissociation constant for NiO_2H^{2+} is 3.2 ± 0.3). The slight dependence on $[C(NO_2)_4]$ at pH 3.05 is probably associated with the fact that the equilibrium between HO_2 and O_2^- becomes rate determining at low pH. From the data in deaerated solutions a value of $k(Ni^+ + C(NO_2)_4) = (1.4 \pm 0.2) \times 10^9\ M^{-1}\ s^{-1}$ is obtained.

We have no evidence for the reversibility of reaction 23 from either the benzoquinone or tetranitromethane transfer experiments, but cannot rule out this possibility. However, the equilibrium, if it exists, lies well to the right, and we estimate $K_{23} \geqslant 2 \times 10^6\ M^{-1}$.

Concluding Remarks

The data presented here show that molecular oxygen may add to reduced metal ions in some cases, although where the reduced metal ion has very powerful reducing properties electron transfer may be favored. Comparison with stable oxygen complexes of metals in the next higher valency state provides an interesting insight into the role of electron donating ligands (e.g., porphyrin, triphenylphosine, etc.)[3] in the formation of these complexes, and a possible significance of the ligands in many biochemical processes.

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(22) k_{12} was measured from the rate of formation of benzosemiquinone at 410 nm in solutions containing 10^{-2} M Cr^{3+}, 0.5 M *tert*-butyl alcohol, and $(2.5–37.5) \times 10^{-5}$ M $C_6H_4O_2$, pH 3.4, dose ca. 300 rad $pulse^{-1}$ and $I = 0.1$ M. The pseudo-first-order rate constant, k_{obsd}, for the reaction depended on $[C_6H_4O_2]$ according to $k_{obsd} = a + b[C_6H_4O_2]$. b is equated with k_{12}. a, which had a value of $(3 \pm 1) \times 10^3\ s^{-1}$, represents only a very minor pathway, and can probably be identified with the reaction of Cr^{2+} with the *tert*-butyl alcohol peroxy radical.
(23) The fate of HO_2 is uncertain. It may react rapidly with the *tert*-butyl alcohol peroxy radical, in which case it will not absorb appreciably 4.5 ms after the pulse. However, if this reaction is slow a small correction should be applied to the CrO_2^{2+} spectrum, and would give ϵ_{245} 7600 ± 800 $M^{-1}\ cm^{-1}$ and ϵ_{290} 3200 ± 300 $M^{-1}\ cm^{-1}$, assuming $G(HO_2) = 0.6$.
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$$CuO_2^+ + H^+ \rightarrow Cu^{2+} + HO_2$$

The reverse of this was not considered. Recently this has been shown to occur with k = ca. $10^6\ M^{-1}\ s^{-1}$.[39]
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Alkyl Cleavages from Organomercurials. 2. Electron Transfer Process with Hexachloroiridate(IV)

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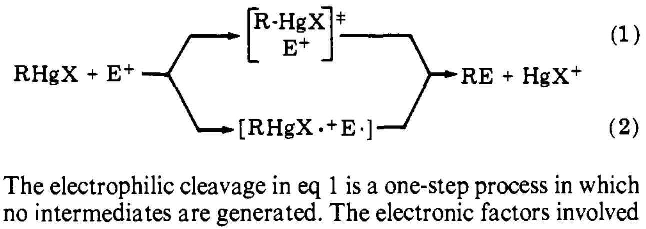
Abstract: Alkyl transfer from organomercury by hexachloroiridate(IV) proceeds by a rate-determining electron transfer process, followed by the facile homolysis of the mercury–alkyl bond. The alkyl radicals so formed are trapped by a second $IrCl_6^{2-}$, either as alkyl chloride via chlorine transfer or alkene via alkyl carbonium ions. All of the mercury products as well as the reduced iridium(III) species are characterized, and the stoichiometry of the cleavage is fully delineated. Alkyl radicals are established as prime intermediates through the ESR observation of nitroxide adducts formed by spin traps and the quantitative scavenging by oxygen. The second-order rate constants k for cleavage of R–HgMe increase in the order: R = Me (1.5×10^{-3}), Et (2.0), i-Pr (2.2×10^2), t-Bu ($1.6 \times 10^3\ M^{-1}\ s^{-1}$). The values of log k correlate well with the energetics of other electron detachment processes, i.e., $R_2Hg \rightarrow R_2Hg\cdot^+ + \epsilon$, such as the vertical ionization potentials and the frequency of the charge transfer bands of tetracyanoethylene complexes. Inner and outer-sphere mechanisms for electron transfer processes in organomercurials are discussed.

Organomercury compounds are involved as reactants or intermediates in a variety of synthetic organic procedures.[1] In a majority of these transformations, the cleavage of the carbon–mercury bond proceeds via an electrophilic mechanism.[2] However, a variety of electrophilic processes have recently been shown to involve prior electron transfer.[3] The mechanistic distinction between an electrophilic cleavage of a carbon-mercury bond and one proceeding via electron transfer is outlined in eq 1 and 2, respectively.



The electrophilic cleavage in eq 1 is a one-step process in which no intermediates are generated. The electronic factors involved in the *transition state* of electrophilic cleavage of organomercurials are discussed in the foregoing study.[4] In contrast, the electron transfer process in eq 2 proceeds by a two-step mechanism in which the transfer of an electron from the mercurial to the electrophile constitutes the rate-limiting reaction. The difference between the two mechanisms lies in the ability of electrophiles to function as one-electron acceptors, i.e., $E^+ + \epsilon \rightarrow E\cdot$. Since many electrophiles are indeed oxidants, the distinction between electrophilic and electron transfer processes is not easily made. Thus, it is not surprising that only a limited number of authenticated examples are extant.[5]

We wish to examine the cleavage of the carbon–mercury bond by an electron transfer process in order to develop diagnostic patterns for such mechanisms in organomercurials. Moreover, it is important to differentiate electron transfer from electrophilic mechanisms in the cleavage of organometals in general, and organomercurials are excellent models for study since they are not commonly considered to participate in electron transfer processes as are their transition metal counterparts. In this study, hexachloroiridate(IV) was chosen for its well-known properties as a one-electron oxidant capable of participating in both outer-sphere and inner-sphere processes.[6] Criteria are developed to distinguish the reaction of organomercurials with hexachloroiridate(IV) from the more conventional electrophilic cleavages.

Results

A complete series of symmetrical as well as unsymmetrical dialkylmercury compounds, that is, R_2Hg and $RHgCH_3$, in which R is methyl, ethyl, isopropyl, and *tert*-butyl, were investigated in this study. All of these organomercurials reacted readily with a solution of hexachloroiridate(IV) in acetic acid or acetonitrile under an inert atmosphere. For example, the addition of diethylmercury to a solution of hexachloroiridate(IV) resulted in the immediate discharge of the red-brown color, followed by partial precipitation of reduced iridium(III) salts.

Products and Stoichiometry. The organic and the mercurial products of the reaction were identified and analyzed quantitatively by NMR spectroscopy and gas liquid chromatography.