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Reactivity of $[Co^{III}W_{12}O_{40}]^{5-}$ with organic radicals in aqueous solution. Evidence for an electron transfer mechanism

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The rate constants for reaction of the [12-tungstocobaltate(III)]$^{5-}$ ion $[Co^{III}W_{12}O_{40}]^{5-}$ in aqueous solution with a large number of carbon-centered cyclic and acyclic radicals, among them radicals of the alkyl, α-hydroxyalkyl, α-alkoxyalkyl, α-amidoalkyl and benzyl type, have been measured by pulse radiolysis. Except for methyl and ethyl radical and α-carboxyalkyl radical anions, the radicals react with rates of the order (1–5) × 10^9 dm^3 mol^{-1} s^{-1}, which corresponds to or is close to diffusion control. From a comparison with oxidants that are able to react by ligand transfer, the oxidant $[Co^{III}W_{12}O_{40}]^{5-}$ is concluded to react by electron transfer.

The [12-tungstocobaltate(III)]$^{5-}$ ion, $[Co^{III}W_{12}O_{40}]^{5-}$ (abbreviated as Co^{III}W in the following),[1] is apparently a perfect outer-sphere one-electron oxidant, not only with respect to inorganic but also towards organic molecules, due to the sheath of the chemically inert oxygen atoms which protect the central ion thus providing a very high degree of substitution-inertness, which means that inner-sphere (ligand-transfer) reactions are very unlikely to take place. For this reason, oxidation with Co^{III}W typically leads to 'clean' chemistry and therefore the ion has frequently been used to generate (by thermal reaction) radical cations of (electron-rich) aromatics, often of the anisole-type, and to study their reactivities.[2-4] Radical *cations* are often transformed to yield *neutral* radicals by substitution (involving a nucleophile), deprotonation or side-chain fragmentation reactions.[5,6] On the basis of the product analysis results,[3,4] these radicals are subsequently oxidized by Co^{III}W, apparently also by an outer-sphere electron transfer (ET) mechanism, to yield the final, non-radical products. Thus, in order to obtain a better understanding of the overall oxidation process of organics by Co^{III}W, it is necessary also to know the rate constants for oxidation of radicals by Co^{III}W. These values so far have not been determined. A further, but related reason for initiating the present study was the hope of obtaining information on structure–reactivity relationships relating to oxidation of organic radicals by Co^{III}W. This is also an important question in connection with the use of (inorganic) oxidants for 'redox titration' of radicals.[7] If the oxidant tends to react by ligand transfer or addition, the distinction between different radicals on the basis of their redox properties would be much more complicated than in the case of an electron-transfer mechanism.†

Results and discussion

Radiolysis of water [eqn. (1)] is a convenient way of producing known amounts of radicals. For work under oxidizing conditions, e_{aq}^- is commonly converted to yield OH$^\cdot$ by irradiating N$_2$O-saturated aqueous solutions.

$$H_2O \longrightarrow e_{eq}^-, OH^\cdot, H^\cdot, H^+ \qquad (1)$$

$$e_{aq}^- + N_2O + H_2O \longrightarrow N_2 + OH^- + OH^\cdot \qquad (2)$$

The radicals from the water radiolysis (1) can easily be converted into secondary radicals. For example, if e_{aq}^- reacts with $S_2O_8{}^{2-}$, the strong oxidant $SO_4{}^{\cdot-}$ is formed.

$$e_{aq}^- + S_2O_8{}^{2-} \longrightarrow SO_4{}^{2-} + SO_4{}^{\cdot-} \qquad (3)$$

In this study, the organic radicals were produced by four different methods [eqns. (4)–(7)]: addition of OH$^\cdot$ to dialkyl sulfoxides followed by fragmentation of the adduct to yield sulfinic acids and alkyl radicals;[10] hydrogen atom abstraction by OH$^\cdot$ and H$^\cdot$ from aliphatics; addition of OH$^\cdot$ to aromatics or C–C double bonds; and oxidative decarboxylation of carboxylic acids with $SO_4{}^{\cdot-}$.‡

$$OH^\cdot + R_2SO \longrightarrow RSO_2{}^- + H^+ + R^\cdot \qquad (4)$$

$$OH^\cdot(H^\cdot) + RH \longrightarrow H_2O(H_2) + R^\cdot \qquad (5)$$

$$OH^\cdot + Ar \longrightarrow Ar\text{–}OH^\cdot \qquad (6)$$

$$SO_4{}^{\cdot-} + RCO_2{}^- + CO_2 + R^\cdot \qquad (7)$$

The reactions of the radicals R$^\cdot$ with Co^{III}W (E° = 1.01 V *vs.* NHE), described by eqn. (8), were studied by monitoring the absorption of its 390 nm band (ε = 1.3 × 10^3 dm^3 mol^{-1} cm^{-1}), the reaction resulting in a bleaching of that absorption.

$$R^\cdot + Co^{III}W_{12}O_{40}{}^{5-} \longrightarrow [R^+] + [Co^{II}W_{12}O_{40}]^{6-} \qquad (8)$$

With the concentration of the radicals produced by the irradiation pulse being in the 10^{-6} dm^3 mol^{-1} range, by working under conditions such that Co^{III}W ⩾ 10^{-4} dm^3 mol^{-1}, the depletion of Co^{III}W proceeds under psuedo-first-order conditions. The rate constants k (dm^3 mol^{-1} s^{-1}) for reaction of the radicals R$^\cdot$ with Co^{III}W are then given by the slopes of plots of the rates k_{obs} (s^{-1}) of depletion of the oxidant *versus* its concentration. The rate constants thus obtained, using the radical production methods described in eqns. (4)–(7), are collected in Table 1.

Concerning the simple alkyl radicals Me$^\cdot$ to Bu$^{t\cdot}$, it is evident from Table 1 that k increases dramatically with branching at C$_\alpha$, or, more specifically, with decreasing ionization potential of the radical.[11] This contrasts with the reactions[8] of the weaker oxidant $[Ir^{IV}Cl_6]^{2-}$ with the alkyl radicals (see Table 1), where the reactivity increases by less than a factor of 4 on going from

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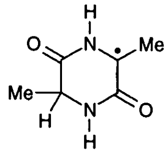
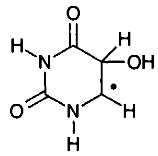
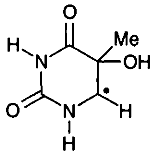
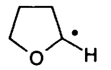
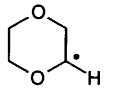
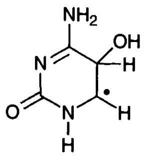
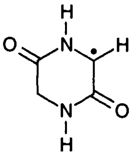
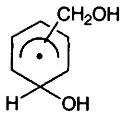
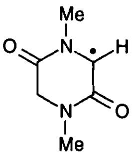
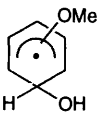
† For example, in the case of reaction of $Ir^{IV}Cl_6{}^{2-}$ (E° = 0.87 V *vs.* NHE) with the weak 'reductant' CH$_3{}^\cdot$, exclusive ligand transfer occurs, *i.e.*, CH$_3$Cl is formed in 100% yield (see ref. 8). In the case of reaction with the less oxidizing but more substitution-inert $[Fe^{III}(CN)_6]^{3-}$ (E° = 0.36 V *vs.* NHE), 20% CH$_3$CN is produced.[9]

‡ The rate constant for reaction of $SO_4^{\cdot-}$ with Co^{III}W is ⩽10^7 dm^3 mol^{-1} s^{-1}. On this basis, Co^{III}W does not compete efficiently with RCO$_2{}^-$ for $SO_4{}^{\cdot-}$.

Table 1 Rate constants $k/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ for reduction of $\mathrm{Co^{III}W}$[a] by carbon-centred radicals $\mathrm{R^{\bullet}}$ in aqueous solution (pH ≈ 6) at 20 ± 2 °C. Comparison with values[b] for reduction of $\mathrm{[Ir^{IV}Cl_6]^{2-}}$

Radical $\mathrm{R^{\bullet}}$	Notes	$k(\mathrm{Co^{III}W})$	$k[\mathrm{Ir^{IV}Cl_6}^{2-}]$[b]	Radical $\mathrm{R^{\bullet}}$	Notes	$k(\mathrm{Co^{III}W})$
$\mathrm{CH_3^{\bullet}}$	*c*	$< 10^5$	1.2×10^9			
$\mathrm{CH_3CH_2^{\bullet}}$	*c*	2.0×10^6	3.1×10^9			
$\mathrm{(CH_3)_2CH^{\bullet}}$	*c*	1.3×10^9	3.6×10^9			
$\mathrm{(CH_3)_3C^{\bullet}}$	*c*	3.3×10^9	3.8×10^9		*i*	2.2×10^9
$\mathrm{PhCH_2^{\bullet}}$	*d*	5.8×10^8	1.8×10^{9}[e]			
$\mathrm{Ph_2CH^{\bullet}}$	*d*	2.4×10^9	1.6×10^{9}[e]			
$\mathrm{Ph_3C^{\bullet}}$	*d*, *f*	5.5×10^9	1.3×10^{9}[e]			
$\mathrm{e_{aq}^{-}}$	*g*	1.3×10^{10}	1×10^{10}[h]			
$\mathrm{CO_2^{\bullet -}}$	*i*	3.3×10^8	1.7×10^9			
$\mathrm{HOCH_2^{\bullet}}$	*i*	2.4×10^9	6.0×10^9			
$\mathrm{HOCH^{\bullet}CH_3}$	*i*	3.9×10^9	4.5×10^9			
$\mathrm{HOC^{\bullet}(CH_3)_2}$	*i*	4.0×10^9	4.7×10^9			
$\mathrm{\overline{CH_2(CH_2)_4}\dot{C}OH}$	*i*	2.0×10^9			*l*	3.1×10^9
$\mathrm{HOCH^{\bullet}CH_2OH}$	*i*	3.0×10^9				
$\mathrm{HOCH^{\bullet}CO_2^{-}}$	*i*	1.9×10^8	2×10^9			
$\mathrm{HOC^{\bullet}(CH_3)CO_2^{-}}$	*i*	2.2×10^8				
$\mathrm{HOC^{\bullet}(CH_3)C(O)OCH_3}$	*i*	1.1×10^9				
$\mathrm{HOC^{\bullet}(CH_3)C(O)NH_2}$	*i*	1.8×10^9				
$\mathrm{CH_3OCH_2^{\bullet}}$	*i*	3.1×10^9	6.5×10^9			
$\mathrm{CH_3CH_2OCH^{\bullet}CH_3}$	*i*	3.3×10^9	5.7×10^9			
$\mathrm{(CH_3)_2CHOC^{\bullet}(CH_3)_2}$	*i*	3.7×10^9	3.6×10^9		*l*	3.2×10^9
	*i*	5.8×10^9				
	*i*	4.1×10^9	5.4×10^9		*l*	4.4×10^9
$\mathrm{PhC^{\bullet}(OCH_3)_2}$	*k*	4.3×10^9				
	*i*	1.2×10^9			*l*	1.6×10^9
	*i*	3.3×10^9			*l*	3.4×10^9

[a] Determined by monitoring the rate of depletion of the 390 nm band of $\mathrm{Co^{III}W}$ as a function of $\mathrm{[Co^{III}W]}$. The error limits for k are to within 10%. [b] From ref. 8. [c] Radical produced by reaction of $\mathrm{OH^{\bullet}}$ with the corresponding dialkyl sulfoxide [eqn. (4)]. [d] Radical formed by reaction of $\mathrm{SO_4^{\bullet -}}$ with the corresponding phenylacetic acid [eqn. (7)]. [e] This work. [f] Monitored at 390 and at 420 nm (formation of $\mathrm{Ph_3C^+}$). $\mathrm{Ph_3C^+}$ decays with $1.5 \times 10^5\ \mathrm{s^{-1}}$ (at $\mathrm{[Co^{III}W]} \geqslant 2 \times 10^{-4}\ \mathrm{dm^3\ mol^{-1}}$). [g] Monitored at 390 and 650 nm ($\mathrm{e_{aq}^{-}}$). [h] From ref. 15. [i] Radical produced by hydrogen atom abstraction from R–H by $\mathrm{OH^{\bullet}}$ [eqn. (5)]. [k] Radical produced by 248 nm photolysis of $\mathrm{PhC(O)C(OCH_3)_2Ph}$. [l] Radical produced by $\mathrm{OH^{\bullet}}$ addition [eqn. (6)].

$\mathrm{Me^{\bullet}}$ to $\mathrm{Bu^{t\bullet}}$. If a Taft plot is constructed from the points for $\mathrm{Et^{\bullet}}$ and $\mathrm{Pr^{i\bullet}}$ (the point for $\mathrm{Bu^{t\bullet}}$ is neglected because the value is probably limited by diffusion), the Taft ρ^* value for reaction (8) is found to be −28,§ which shows the enormous sensitivity of that reaction with respect to the alkyl substituent at $\mathrm{C_\alpha}$ {for comparison, in the reaction of $\mathrm{Me^{\bullet}}$ to $\mathrm{Pr^{i\bullet}}$ with the much weaker oxidant $\mathrm{[Fe(CN)_6]^{3-}}$, ρ^* is only −13}.[8] The higher sensitivity of the stronger oxidant $\mathrm{Co^{III}W}$ would constitute a violation of the reactivity–selectivity principle if the mechanism of these oxidation reactions were the same. In the case of the reaction of $\mathrm{[Fe(CN)_6]^{3-}}$ with $\mathrm{Me^{\bullet}}$, there is some ligand transfer, as evidenced by the formation of acetonitrile.[9] The highly negative ρ^* for the case of $\mathrm{Co^{III}W}$ may thus be understood in terms of an exclusive or certainly predominant electron transfer mechanism.

The benzyl radicals, $\mathrm{PhCH_2^{\bullet}}$, $\mathrm{Ph_2CH^{\bullet}}$ and $\mathrm{Ph_3C^{\bullet}}$ behave towards $\mathrm{Co^{III}W}$ in a way very similar to that exhibited by the alkyl radicals described above. Interesting again is the comparison with $\mathrm{[Ir^{IV}Cl_6]^{2-}}$: this *weaker* oxidant is *less* selective than the stronger one, $\mathrm{Co^{III}W}$. As above, the explanation must be in terms of the difference in mechanism: electron transfer in the case of $\mathrm{Co^{III}W}$ and (partial) ligand transfer in the case of $\mathrm{[Ir^{IV}Cl_6]^{2-}}$.

Concerning the α-hydroxyalkyl radicals, the simplest one, $\mathrm{HOCH_2^{\bullet}}$, reacts already with a rate close to the diffusion limit in water ($\approx 5 \times 10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$), therefore, there is little increase in reactivity in going to the more easily oxidized 'branched' radicals such as $\mathrm{HOC^{\bullet}(CH_3)_2}$. If a carboxylate group is introduced at $\mathrm{C_\alpha}$, the rate constants drop by an order of magnitude. Since this cannot be an electronic effect (the Taft σ^*

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§ This is probably an upper limit, since the value for $\mathrm{Pr^{i\bullet}}$ is already likely to be somewhat 'depressed' by diffusion.

of CO_2^- is close to zero), it must be due to electrostatic repulsion between the *penta*-anion of $Co^{III}W$ and the negatively charged radicals. This also relates to the strongly reducing radical $CO_2^{\bullet -}$, which is typically highly reactive [$k \approx (1–5) \times 10^9$ dm^3 mol^{-1} s^{-1}] with *un*charged or cationic oxidants.[12] In agreement with the charge effect being responsible for the reduction in reactivity is the fact that the (neutral) 'ester' and 'amide' radicals, $HOC^{\bullet}(CH_3)C(O)OCH_3$ and $HOC^{\bullet}(CH_3)$-$C(O)NH_2$, show a higher reactivity, although the ester and amide functions are electron-withdrawing, in contrast with the carboxylate function.

In view of the charge effect on the rate constants, it is interesting that the hydrated electron, e_{aq}^-, has a *very high* reactivity with $Co^{III}W$ ($k = 1.3 \times 10^{10}$ dm^3 mol^{-1} s^{-1}, see Table 1).

The α-*alkoxy*alkyl radicals have a reactivity almost identical with that of the α-*hydroxy*alkyl radicals. Again, the rate-enhancing effect of α-branching is visible. This is also the case with the radicals from the cyclic amides, glycine- and alanine-anhydride. Concerning the radicals formed by addition of $OH^{\bullet}$ to uracil, thymine and cytosine, respectively, their reactivity increases in this order, which is in agreement with their electron-donating power as previously determined[13] and recently confirmed by MO calculations.[14]

In conclusion, it has been found that the rate constants for reaction of carbon-centered neutral radicals with the oxidant $Co^{III}W$ in aqueous solution are typically $(1–5) \times 10^9$ dm^3 mol^{-1} s^{-1}, *i.e.* close to or equal to the diffusion-controlled limit. In the series of the simple alkyl radicals $Me^{\bullet}$ to $Bu^{t\bullet}$, only the reactivity of $Me^{\bullet}$ and $Et^{\bullet}$ is below this limit. From the very strong dependence of the rate constant on the structure of the radical in this family ($\rho^* \leqslant -28$), it is concluded that these oxidation reactions occur through an electron-transfer mechanism.

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