Formation of Chromium–Carbon Bonds in Aqueous Solution; A Pulse Radiolytic Study

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Summary The specific rates of reaction of several aliphatic radicals with Cr^{2+} in aqueous solution were measured and correlated with the unpaired electron density on the reacting carbon atom.

A SERIES of compounds with the general formula $(H_2O)_5$-CrL^{2+}, where L is an aryl or alkyl group, and containing a σ-chromium–carbon bond has been reported recently.[1–4] The absorption spectra and the mechanism of decomposition of many of these complexes have been studied.[1–4] It has been suggested that the mechanism of formation of these complexes in solutions containing an aryl or alkyl halide and

$Cr(H_2O)_6^{2+}$ involves the formation of an organic radical which then reacts with $Cr(H_2O)_6^{2+}$.[2] Radicals formed by hydrogen abstraction from an organic molecule have been shown to react with $Cr(H_2O)_6^{2+}$ forming complexes containing a chromium–carbon bond.[4] However, due to the experimental techniques used in these studies, the specific rates of reaction of the organic radicals with $Cr(H_2O)_6^{2+}$ were not measured. We report several of these rates measured by a pulse radiolytic technique.

The specific rates of formation of and spectral data for chromium–carbon bonds[a]

Reacting radical	k ($M^{-1}\,s^{-1}$)	$\lambda_{max}(1)$[c] (nm)	$\epsilon_{max}(1)$[d] ($M^{-1}\,cm^{-1}$)	$\lambda_{max}(2)$[c] (nm)	$\epsilon_{max}(2)$[d] ($M^{-1}\,cm^{-1}$)	a_{α}^{H}[e]
$\dot{C}H_2CO_2H$	$2{\cdot}5 \times 10^8$	273	960	395	*ca.* 90	21·8
$\dot{C}H_2OH$	$1{\cdot}6 \times 10^8$	282	2·400	392	570	17·6
$CH_3\dot{C}HOH$	$7{\cdot}9 \times 10^7$	296	2·800	396	680	15·4
$(CH_3)_2\dot{C}OH$	$5{\cdot}1 \times 10^7$	311	2·500	407	700	—
$CH_3\dot{C}HOCH_2CH_3$	$3{\cdot}4 \times 10^7$	291	2·160	390	490	13·8

[a] All solutions were saturated with Ar and contained 0·25—0·50 M of the organic solute, 1—10 × 10^{-4}M $Cr(H_2O)_6^{2+}$ and 0·1—1·0M $HClO_4$. [b] Standard deviation ± 15%. [c] Determined by measuring with a Cary 17 Spectrophotometer, accuracy ±2 nm. [d] Determined by the pulse radiolytic technique accuracy ±15%. [e] Hyperfine constants for the e.s.r. splitting by the α hydrogens. Values taken from refs. 8—10.

Argon saturated solutions containing 0·25—0·50M of an organic solute, 1—10 × 10^{-4}M $Cr(H_2O)_6^{2+}$ and 0·1—1M $HClO_4$ have been irradiated. Pulses of 1·2—3·0 × 10^{19} eV l^{-1}, from a linear electron accelerator were used, the experimental procedure has been described elsewhere in detail.[5,6] Under these conditions both hydroxyl radicals and hydrogen atoms, formed by the pulse, react with the organic solutes and not with the $Cr(H_2O)_6^{2+}$, as shown in the reactions (1) and (2).

$$OH + RH \rightarrow R\cdot + H_2O \qquad (1)$$

$$H + RH \rightarrow R\cdot + H_2 \qquad (2)$$

The specific rates of these reactions as well as the nature of the radicals produced are known.[7,8] The radicals $\dot{C}H_2OH$, $CH_3{\cdot}\dot{C}HOH$, $(CH_3)_2\dot{C}OH$, $CH_3\dot{C}HOCH_2CH_3$, and $\dot{C}H_2CO_2H$ are formed within less than 3 μ s from the end of the pulse.

The specific rates of reaction of these radicals with the $Cr(H_2O)_6^{2+}$ were determined spectrophotometrically by following the occurence of chromium–carbon bond absorption[4] (see Table). The absorption spectra of the products were determined both immediately after the formation reaction ended, and several minutes later in a Cary 17 spectrophotometer. Because of the instability of the products the absolute extinction coefficients were measured only by pulse radiolysis.[4] In all cases three absorption peaks were observed at *ca.* 290, 390, and 560 nm. The data for the first two peaks are summarized in the Table. The third peak could not be accurately measured because of small absorption coefficients.

The specific rates of reaction indicate fast but not diffusion controlled reactions. The effect of the structure of the radical on its specific rate of reaction with the $Cr(H_2O)_6^{2+}$ is therefore believed to be indicative of the ease of formation of the σ-chromium–carbon bond. Factors expected to affect the specific rate of formation of such a bond are: (i) The probability that the unpaired electron will be located on the carbon atom; the specific rate of reaction is expected to vary directly with this probability. (ii) As the σ-bond formed contains an e_g electron of the chromium atom, the location of the unpaired electron in a non-bonding *p*-orbital rather than in a resonance stabilized π-system would favour reaction. (iii) Steric hindrance by groups bound to the α-carbon may be expected to slow down the reaction.

The order of reactivity of the radicals towards $Cr(H_2O)_6^{2+}$, $\dot{C}H_2CO_2H > \dot{C}H_2OH > CH_3\dot{C}HOH > (CH_3)_2\dot{C}OH > CH_3\text{-}\dot{C}HOCH_2CH_3$ is in agreement with the order of spin densities of the unpaired electron on the α carbon atom calculated from the hyperfine splitting constants measured by e.s.r.[6–10] For the radicals $\dot{C}H_2OH$, $CH_3\dot{C}HOH$ and $(CH_3)_2\dot{C}OH$ the same order was also indicated by the basic dissociation constants of the hydroxylic group.[11] It has been suggested that this order of increased probability of locating the unpaired electron on the carbon atom is accompanied by a larger non-bonding character of the orbital in which it is located.[12] Our results show that the major factors influencing the specific rate of reaction of $Cr(H_2O)_6^{2+}$ with an organic radical are the probability of locating the unpaired electron on a given carbon atom and the nature of its orbital. The magnitude of effects observed being too great to be explained only by steric hindrance.

The reactivities of the $\dot{C}H_2CO_2H$, $\dot{C}H_2OH$, $CH_3\dot{C}HOH$, and $(CH_3)_2\dot{C}OH$ radicals are in the same order as the stability of the trivalent chromium complexes formed in the reaction.[4,13] The $CH_3\dot{C}HOCH_2CH_3$ radical[4] is an exception in **this** respect.

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