

Kinetics of the Capture of Methyl Radicals by Carbon Monoxide in Aqueous Solution

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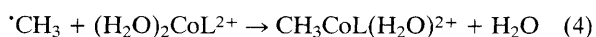
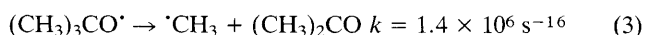
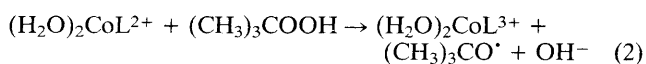
The title reaction has a rate constant of $(2.0 \pm 0.3) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25 °C, which is fast enough to make it a useful route for C–C bond formation even at ambient temperatures and pressures.

The gas phase reaction of $\text{CH}_3\cdot$ with CO ,¹ eqn. (1), has forward and reverse rate constants of $k_1 = 6.5 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_{-1} = 7.3 \text{ s}^{-1}$ at 25 °C. It has been assumed that the solution and gas phase values of k_1 are similar,² but some other work indicated that reaction (1) is 'exceedingly fast' in

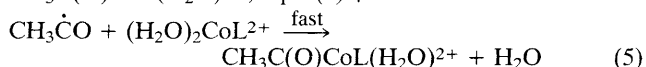


solution.³ The apparent controversy and the potential importance of reaction (1) as a C–C bond forming step in organic and organometallic synthesis prompted us to study the solution reaction. A direct determination by standard methods would be difficult in view of the low molar absorptivities of all the species involved, and thus a chemical competition method was devised.

Methyl radicals were generated by a Fenton-type reaction between Bu^tOOH and either of two macrocyclic cobalt complexes $(\text{H}_2\text{O})_2\text{CoL}^{2+}$ ($\text{L}^1 = 1,4,8,11$ -tetraazacyclotetradecane, $\text{L}^2 = \text{meso-}5,7,7,12,14,14$ -hexamethyl-1,4,8,11-tetraazacyclotetradecane), eqn. (2)–(3), at pH 1–2.[†] In argon-saturated solutions in the absence of CO reaction (3) was followed exclusively by the capture of $\cdot\text{CH}_3$ by $(\text{H}_2\text{O})_2\text{CoL}^{2+}$ in the concentration ranges $[(\text{H}_2\text{O})_2\text{CoL}^{2+}] = 0.1$ – 1 mmol dm^{-3} (always in an excess), $[\text{Bu}^t\text{OOH}] = 0.05$ – 0.4 mmol dm^{-3} , eqn. (4).^{4,5}



Under an atmosphere of CO, the competition between $(\text{H}_2\text{O})_2\text{CoL}^{2+}$ and CO for $\cdot\text{CH}_3$, eqns. (1) and (4), resulted in the formation of two different organocobalt complexes, the known $\text{CH}_3\text{CoL}(\text{H}_2\text{O})^{2+}$ ^{4,5} and a novel acetyl complex $\text{CH}_3\text{C}(\text{O})\text{CoL}(\text{H}_2\text{O})^{2+}$, eqn. (5).[‡]



[†] The values of k_2 are 52.0 (L^1) and 11.4 (L^2) $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, irrespective of whether the reactions are run under Ar or Co.

[‡] Reaction (5) probably has a rate constant of $(1\text{--}5) \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, similar to reactions of these cobalt complexes with alkyl radicals,⁴ and is therefore fast in comparison with other possible reactions of the radicals under experimental conditions.

The yields of acetylcobalt were determined spectrophotometrically after the reduction by Cr^{2+} of the strongly absorbing $(\text{H}_2\text{O})_2\text{CoL}^{3+}$, formed in reaction (2), to the weakly absorbing $(\text{H}_2\text{O})_2\text{CoL}^{2+}$. These experiments used CO-saturated solutions ($[\text{CO}] = 0.96 \text{ mmol dm}^{-3}$)⁸ and several concentrations of $(\text{H}_2\text{O})_2\text{CoL}^{2+}$ (0.05 – 1.0 mmol dm^{-3} for L^1 , 0.1 – 0.5 mmol dm^{-3} for L^2) and Bu^tOOH (0.02 – 0.4 mmol dm^{-3} for L^1 , 0.04 – 0.2 mmol dm^{-3} for L^2). The data were fitted to eqn. (6),[§] which yielded $k_1 = (2.3 \pm 0.1) \times 10^6$ ($\text{L} = \text{L}^1$) and $(1.8 \pm 0.1) \times 10^6$ ($\text{L} = \text{L}^2$) $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, giving an average value of $(2.0 \pm 0.3) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

$$[\text{CH}_3\text{C}(\text{O})\text{CoL}(\text{H}_2\text{O})^{2+}]_{\infty} = - (k_1/2k_4) [\text{CO}]_{\text{av.}}$$

$$\ln \left\{ 1 - \frac{[\text{Bu}^t\text{OOH}]_0}{0.5[(\text{H}_2\text{O})_2\text{CoL}^{2+}]_0 + (k_1/2k_4) [\text{CO}]_{\text{av.}}} \right\} \quad (6)$$

This confirms the reaction scheme of eqns. (1), (4), (5), and thus the validity of our approach to the determination of k_1 . Specifically, the most probable alternative scheme, whereby $\cdot\text{CH}_3$ reacts rapidly with small (but undetected) amounts of a

[§] Eqn. (6) takes into account the fact that the concentration of $(\text{H}_2\text{O})_2\text{CoL}^{2+}$ changes significantly during the course of each experiment, whereas that of CO remains sufficiently constant that an average value suffices. Thus $[(\text{H}_2\text{O})_2\text{CoL}^{2+}]_t = [(\text{H}_2\text{O})_2\text{CoL}^{2+}]_0 - 2[\text{CH}_3\text{CoL}(\text{H}_2\text{O})^{2+}]_t - 2[\text{CH}_3\text{C}(\text{O})\text{CoL}(\text{H}_2\text{O})^{2+}]_t$ and $[\text{CH}_3\text{CoL}(\text{H}_2\text{O})^{2+}]_{\infty} + [\text{CH}_3\text{C}(\text{O})\text{CoL}(\text{H}_2\text{O})^{2+}]_{\infty} = [\text{Bu}^t\text{OOH}]_0$. Subscripts 0 and ∞ are used for initial and final concentrations, and t for all the intermediate ones.

Thus, according to eqns. (1), (4) and (5), and denoting LCoCOCH_3^{2+} as A and LCoCH_3^{2+} as B:

$$\frac{d[\text{B}]/dt}{d[\text{A}]/dt} = \frac{k_4[\text{LCo}^{2+}]}{k_1[\text{CO}]} = \frac{k_4([\text{LCo}^{2+}]_0 - 2[\text{A}] - 2[\text{B}])}{k_1[\text{CO}]_{\text{av.}}}$$

$$\frac{d[\text{B}]}{d[\text{A}]} + \frac{2k_4[\text{B}]}{k_1[\text{CO}]_{\text{av.}}} = \frac{k_4[\text{LCo}^{2+}]_0}{k_1[\text{CO}]_{\text{av.}}} - \frac{2k_4[\text{A}]}{k_1[\text{CO}]_{\text{av.}}}$$

If $2k_4/k_1[\text{CO}]_{\text{av.}} = a$ and $k_4[\text{LCo}^{2+}]_0/k_1[\text{CO}]_{\text{av.}} = b$, then

$$\frac{d[\text{B}]}{d[\text{A}]} + a[\text{B}] = b - a[\text{A}]$$

Multiplication of both sides by $e^{a[\text{A}]}$ and integration yields

$$[\text{B}]e^{a[\text{A}]} = b/a e^{a[\text{A}]} - e^{a[\text{A}]} ([\text{A}] - 1/a)$$

Substitution of the limits ($[\text{A}] = [\text{B}] = 0$ at $t = 0$, and $[\text{A}] = \text{A}_{\infty}$, $[\text{B}] = [\text{B}]_{\infty}$ at time ∞ , and $[\text{B}]_{\infty} + [\text{A}]_{\infty} = [\text{Bu}^t\text{OOH}]_0$, yields the final eqn. (6).

cobalt-CO adduct, is ruled out. For a given L such a scheme would require that a constant percentage of the organocobalt product be present as the acetyl complex at constant [CO]. This is clearly not the case, and the yield of $\text{CH}_3\text{C}(\text{O})\text{-CoL}(\text{H}_2\text{O})^{2+}$ increases with decreasing $[(\text{H}_2\text{O})_2\text{CoL}^{2+}]$ as described by the reaction scheme and eqn. (6).

The value of k_1 is much larger in water than in the gas phase because solvation stabilises the polar acetyl radical. This also implies that k_1 might decrease significantly in less polar solvents.

The solid $[\text{CH}_3\text{C}(\text{O})\text{CoL}(\text{H}_2\text{O})](\text{ClO}_4)_2$ was prepared with both L^1 and L^2 by visible light photolysis (300 W sun lamp) of an ice-cold 1 mmol dm^{-3} solution of $\text{CH}_3\text{CoL}(\text{H}_2\text{O})^{2+}$ under constant bubbling of CO. The complexes were purified by ion exchange and the yellow salts precipitated by the addition of solid NaClO_4 . For $\text{L} = \text{L}^1$, λ_{max} 452 nm (ϵ 90.7 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) and 319 (1190); ^1H NMR, δ 1.48 (CH_3), ^{13}C NMR, δ 32.7 (CH_3). For $\text{L} = \text{L}^2$, λ_{max} 472 nm (ϵ 81.0) and 324 (834). The presence of the CH_3CO group, (and specifically not its hydrated form) was established by laser flash photolysis of $\text{CH}_3\text{C}(\text{O})\text{CoL}^1(\text{H}_2\text{O})^{2+}$ ($\lambda_{\text{irradiation}}$ 490 nm). The CH_3CO was identified by its known rate of hydration ($2 \times 10^4 \text{ s}^{-1}$)⁷ and by the subsequent reaction of $\text{CH}_3\dot{\text{C}}(\text{OH})_2$ with $\text{C}(\text{NO}_2)_4$.⁷

The clean photochemistry of the acetyl complex makes it an excellent source of acetyl radicals, which until now had to be

prepared by pulse radiolysis of CH_3CHO for direct kinetic studies in aqueous solutions.⁷

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- 8 *Solubility Data Series, Carbon Monoxide*, ed. R. W. Cargill, Pergamon Press, Oxford, New York, 1990, p. 2. It was assumed that the presence of submillimolar concentrations of $(\text{H}_2\text{O})_2\text{CoL}^{2+}$ and Bu^1OOH had no effect on the solubility of CO in H_2O .