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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 ± 0.3) × 10^6 $dm^3\ mol^{-1}\ s^{-1}$ 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 $CH_3^{\bullet}$ with CO,[1] eqn. (1), has forward and reverse rate constants of $k_1 = 6.5 \times 10^3$ $dm^3\ mol^{-1}\ s^{-1}$ and $k_{-1} = 7.3\ s^{-1}$ 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.

$$^{\bullet}CH_3 + CO \rightleftarrows CH_3\dot{C}O \tag{1}$$

Methyl radicals were generated by a Fenton-type reaction between Bu^tOOH and either of two macrocyclic cobalt complexes $(H_2O)_2CoL^{2+}$ (L^1 = 1,4,8,11-tetraazacyclotetradecane, L^2 = *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 $^{\bullet}CH_3$ by $(H_2O)_2CoL^{2+}$ in the concentration ranges $[(H_2O)_2CoL^{2+}]$ = 0.1–1 mmol dm^{-3} (always in an excess), $[Bu^tOOH]$ = 0.05–0.4 mmol dm^{-3}, eqn. (4).[4,5]

$$(H_2O)_2CoL^{2+} + (CH_3)_3COOH \rightarrow (H_2O)_2CoL^{3+} + (CH_3)_3CO^{\bullet} + OH^- \tag{2}$$

$$(CH_3)_3CO^{\bullet} \rightarrow {}^{\bullet}CH_3 + (CH_3)_2CO \quad k = 1.4 \times 10^6\ s^{-1}\,\text{[6]} \tag{3}$$

$$^{\bullet}CH_3 + (H_2O)_2CoL^{2+} \rightarrow CH_3CoL(H_2O)^{2+} + H_2O \tag{4}$$

Under an atmosphere of CO, the competition between $(H_2O)_2CoL^{2+}$ and CO for $^{\bullet}CH_3$, eqns. (1) and (4), resulted in the formation of two different organocobalt complexes, the known $CH_3CoL(H_2O)^{2+}$[4,5] and a novel acetyl complex $CH_3C(O)CoL(H_2O)^{2+}$, eqn. (5).‡

$$CH_3\dot{C}O + (H_2O)_2CoL^{2+} \xrightarrow{\text{fast}} CH_3C(O)CoL(H_2O)^{2+} + H_2O \tag{5}$$

The yields of acetylcobalt were determined spectrophotometrically after the reduction by Cr^{2+} of the strongly absorbing $(H_2O)_2CoL^{3+}$, formed in reaction (2), to the weakly absorbing $(H_2O)_2CoL^{2+}$. These experiments used CO-saturated solutions ([CO] = 0.96 mmol dm^{-3})[8] and several concentrations of $(H_2O)_2CoL^{2+}$ (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 $k_1 = (2.3 \pm 0.1) \times 10^6$ ($L = L^1$) and $(1.8 \pm 0.1) \times 10^6$ ($L = L^2$) $dm^3\ mol^{-1}\ s^{-1}$, giving an average value of $(2.0 \pm 0.3) \times 10^6$ $dm^3\ mol^{-1}\ s^{-1}$.

$$[CH_3C(O)CoL(H_2O)^{2+}]_\infty = -\,(k_1/2k_4)\,[CO]_{av.}\ \ln\left\{1 - \frac{[Bu^tOOH]_o}{0.5[(H_2O)_2CoL^{2+}]_o + (k_1/2k_4)\,[CO]_{av.}}\right\} \tag{6}$$

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 $^{\bullet}CH_3$ reacts rapidly with small (but undetected) amounts of a

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

‡ Reaction (5) probably has a rate constant of (1–5) × 10^7 $dm^3\ mol^{-1}\ s^{-1}$, 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.

§ Eqn. (6) takes into account the fact that the concentration of $(H_2O)_2CoL^{2+}$ changes significantly during the course of each experiment, whereas that of CO remains sufficiently constant that an average value suffices. Thus $[(H_2O)_2CoL^{2+}]_t = [(H_2O)_2CoL^{2+}]_o - 2[CH_3CoL(H_2O)^{2+}]_t - 2[CH_3C(O)CoL(H_2O)^{2+}]_t$ and $[CH_3CoL(H_2O)^{2+}]_\infty + [CH_3C(O)Co(L)(H_2O)^{2+}]_\infty = [Bu^tOOH]_o$. Subscripts o 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:

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

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

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

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

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

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

Substitution of the limits ([A] = [B] = 0 at t = 0, and $[A] = A_\infty$, $[B] = [B]_\infty$ at time ∞, and $[B]_\infty + [A]_\infty = [Bu^tOOH]_o$, 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 $CH_3C(O)$-$CoL(H_2O)^{2+}$ increases with decreasing $[(H_2O)_2CoL^{2+}]$ 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 $[CH_3C(O)CoL(H_2O)](ClO_4)_2$ 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 $CH_3CoL(H_2O)^{2+}$ 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 $L = L^1$, λ_{max} 452 nm (ε 90.7 $dm^3\ mol^{-1}\ cm^{-1}$) and 319 (1190); ^1H NMR, δ 1.48 (CH_3), ^{13}C NMR, δ 32.7 (CH_3). For $L = L^2$, 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 $CH_3C(O)CoL^1(H_2O)^{2+}$ ($\lambda_{irradiation}$ 490 nm). The CH_3CO was identified by its known rate of hydration ($2 \times 10^4\ s^{-1}$)[7] and by the subsequent reaction of $CH_3C(OH)_2$ with $C(NO_2)_4$.[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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