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Photochemical Generation of Metastable Methylcopper Complexes. Oxidation–Reduction of Methyl Radicals by Copper Complexes

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Methyl radicals, generated by flash irradiations of $Co(NH_3)_5OCOCH_3^{2+}$, were intercepted with Cu^{2+}(aq) and Cu^+(aq) ions. Metastable species, formed in these reactions, were assigned as $CuCH_3^{2+}$ ($\lambda_{max} \leq 350$ nm) and $CuCH_3^+$ (λ_{max} 370 nm). A transient, assigned also as $CuCH_3^+$, was observed in irradiations of $CuOCOCH_3^+$. Product yields were measured in order to confirm the nature of the transients.

Introduction

The oxidation–reduction reactions of the free radicals with coordination complexes have been the subject of a large number of studies.[1] Further, a generalized mechanism, for the oxidation of alkyl radicals by copper(II) complexes, was proposed by Kochi and co-workers, eq 1–4.[2a] The oxidation

$$R\cdot + CuX_2 \rightleftharpoons RCuX_2 \qquad (1)$$

$$RCuX_2 \rightarrow R(-H) + HX + Cu^IX \qquad (2)$$

oxidative elimination

$$RCuX_2 \rightleftharpoons [RCuX^+,X^-] \rightleftharpoons [R^+,CuX] \xrightarrow{HS} RS + Cu^IX + H^+ \qquad (3)$$

oxidative solvolysis

$$RCuX_2 \rightleftharpoons [R^+,CuX_2] \rightarrow RX + Cu^IX \qquad (4)$$

oxidative displacement

in such a reaction scheme proceeds via a metastable alkylcopper intermediate which is transformed through several competitive channels, eq 2, 3, and 4. However, alternative mechanisms, ligand transfer and/or electron transfer, were proposed by Walling et al.[2b]

Intermediates, namely copper(II)–alkyl species, have not been studied by direct means until recently.[3] The generation of methylcopper complexes in reactions of methyl radicals with Cu(II) and Cu(I) complexes is reported here.

Experimental Section

Photolysis Procedures. The experimental arrangement, used in continuous way photolyses, consisted of a 300-W xenon Varian Eimac lamp combined with a Bausch and Lomb monochromator, collimating filters, and lenses as appropriate to the experiment. Ferrioxalate was used as a primary actinometric reference.[4] Furthermore, the light intensity was frequently tested with $Co(NH_3)_5Br^{2+}$.[5]

Concentrations of the complexes $Co(NH_3)_5OCOCH_3^{2+}$ and $CuOCOCH_3^+$ were adjusted in order to absorb more than 99% of the incident light. Photolyses were carried out in solutions deaerated with either nitrogen streams or vacuum. Three freeze–thaw cycles were used for vacuum deaeration.

Quantum yields were estimated from slopes of the curves product concentration vs. time of irradiation. Values of the slopes were extrapolated to zero time and used for such calculations.

The flash photolysis setup was already described in detail.[6] Pulses of white light with a life span of 30 μs were obtained for stored energies equal to or smaller than 250 J/pulse. Irradiations were carried out in selected spectral regions which were isolated with cutoff filters.[7] In this regard, the irradiation of Cu^{2+}(aq) ions, expected in solutions of this species and $Co(NH_3)_5OCOCH_3^{2+}$, was prevented by using both a 280-nm cutoff filter and concentrations of Cu^{2+}(aq) smaller than 10^{-1} M. Indeed, the irradiation of free acetate ions, present in solutions of $CuOCOCH_3^+$ ions, was avoided with a 260-nm cutoff filter.[7]

Flash energies were varied from 40 to 250 J/pulse in order to produce various transient concentrations. The oxidation of Br^- by $CH_3\cdot$ radicals was used to evaluate the initial concentration of radicals produced per pulse at a given flash output. The species Cu^{2+}(aq) was replaced by 10^{-3} M NaBr in experiments where the source of methyl radicals was $Co(NH_3)_5OCOCH_3^{2+}$ (see above). The concentration of Br_2^-, produced at zero time, was related to the stored flash energy by a constant ($[Br_2^-] = k \times$ (flash energy); $k = 4 \times 10^{-8}$ M/J) for energies in the range 0–250 J/pulse. Reaction kinetics were studied from the dependence of the rate constants and/or reaction half-lives on various substrates and transient concentrations (see Results and Discussion section).

Table I. Products Generated in Reactions of Methyl Radicals with Copper Complexes[a]

Product	Yield I	Yield II
	(a) $CuCH_3^{2+}$ [b]	
CH_3OH	0.073 ± 0.008 (3)	
CH_4	0.014 ± 0.004 (5)	0.095 ± 0.005 (3)
C_2H_6	~0.002 (3)	0.032 ± 0.003 (4)
Co(II)	0.11 ± 0.03 (3)	0.13 ± 0.03 (4)
	(b) $CuCH_3^+$ [c]	
CH_4	0.080 ± 0.004 (5)	
C_2H_6	0.070 ± 0.004 (5)	
CO_2	0.10 ± 0.03 (3)	
Cu(I)	⩽0.003 (3)	

[a] Number of determinations in parentheses. Yields obtained by extrapolation to zero time. [b] Yields of products generated by irradiation of 10^{-2} M $Co(NH_3)_5OCOCH_3^{2+}$: (I) in the presence of 1×10^{-3} M Cu^{2+}(aq), λ_{excit} 254 nm, $I_0 = 8 \times 10^{-5}$ einstein/(L min); (II) in the absence of Cu^{2+}(aq). [c] Yields of products obtained in photolyses of 10^{-2} M $CuOCOCH_3^+$.

Analytical Procedures. Gas products, methane, ethane, and carbon dioxide, were determined by gas chromatography and by mass spectrometry. Methanol was analyzed with chromotropic acid. Concentrations of Cu^{2+}(aq) and Co^{2+}(aq) were respectively determined with 2,4-dimethyl-1,10-phenanthroline[8] and thiocyanate.[9]

Solutions of Cu^+(aq) were handled as indicated elsewhere.[10]

Materials. $[Co(NH_3)_5OCOCH_3](ClO_4)_2$ was prepared according to published procedures.[11] The complex was recrystallized twice from distilled water by addition of 4 M $NaClO_4$.

Solutions of $CuClO_4$ were prepared and handled by reported procedures.[10]

Other materials were reagent grade and used without further purification.

Results and Discussion

Methyl radicals were produced in flash irradiations of 10^{-4} M $Co(NH_3)_5OCOCH_3^{2+}$ in deaerated acidic (10^{-2} M $HClO_4$) solutions by a procedure already suggested by Endicott and Hoffman (see eq 5 and ref 12). Interception of the methyl radicals with 10^{-2} M–2×10^{-1} M $Cu(ClO_4)_2$ produced transient absorptions ($\lambda_{max} \leq 350$ nm) shown in Figure 1a. The initial growth of the transient, Figure 1b, exhibited a first-order dependence on both Cu^{2+}(aq) (10^{-1} M $\geq [Cu^{2+}] \geq 10^{-2}$ M) and methyl radical concentrations. A second-order rate constant, $k = (7.4 \pm 0.6) \times 10^5$ M^{-1} s^{-1}, was obtained for this process. Moreover, the decay of the intermediate obeyed a first-order rate law ($k = (7.2 \pm 0.3) \times 10^2$ s). Flash photolysis of a deaerated solution of Cu^{2+}(aq) (10^{-1} M) did not produce transient absorptions.

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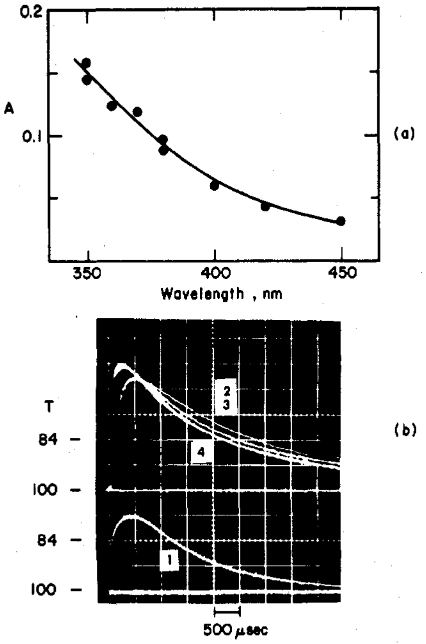

Figure 1. Transient absorptions observed in reactions of methyl radicals and $Cu^{2+}(aq)$ ions ($[Co(NH_3)_5OCOCH_3^{2+}] = 2 \times 10^{-4}$ M; $[HClO_4] = 10^{-2}$ M; $[Cu^{2+}(aq)] = 0.1$ M): (a) spectra obtained with $t = 500$ μs; (b) oscillographic traces monitored at 370 nm for (1) first irradiation, (2) second irradiation, (3) third irradiation, and (4) fourth irradiation; $\lambda_{excit} \geq 240$ nm; energy/flash 250 J.

Continuous way irradiations (λ_{excit} 254 nm; $I_0 = 8 \times 10^{-5}$ einstein/(L min)) were carried out in deaerated solutions containing 10^{-2} M $HClO_4$ and 2×10^{-1} M Cu^{2+}. Methanol and methane were the most abundant reaction products (Table Ia). In this regard, product yields show that a very efficient oxidation of the methyl radicals is achieved under these experimental conditions. Therefore, the intermediate observed in flash photolyses can be assigned as a methylcopper compex, $CuCH_3^{2+}$. Intermediates with a similar nature have been observed by Meyerstein et al. in reactions of carbon-centered radicals and copper(II) complexes.[3] Reactions 5–11 constitute

$$Co(NH_3)_5OCOCH_3^{2+} \xrightarrow[H^+]{h\nu} Co^{2+} + 5NH_4^+ + CO_2 + CH_3\cdot \quad (5)$$

$$CH_3\cdot + CH_3\cdot \rightarrow C_2H_6 \quad (6)$$

$$CH_3\cdot + Co(NH_3)_5OCOCH_3^{2+} \xrightarrow{H^+} CH_4 + Co^{2+} + 4NH_4^+ + NH_3^+ + CH_3CO_2H \quad (7)$$

$$CH_3\cdot + Cu^{2+} \rightarrow CuCH_3^{2+} \quad (8)$$

$$CuCH_3^{2+} \rightarrow Cu^+ + CH_3OH + H^+ \quad (9)$$

$$NH_3^+ \begin{cases} \xrightarrow{NH_3^+} \text{products} & (10) \\ \longrightarrow \text{products} & (11) \end{cases}$$

a possible pathway for formation and decay of such a species. The large yield of CH_4, compared with C_2H_6, seems to indicate that a significant fraction of the methyl radicals is trapped by $Co(NH_3)_5OCOCH_3^{2+}$. Indeed, a rate constant, $k_7 = 4 \times 10^3$ M^{-1} s^{-1}, was reported for reaction 7.[12] A ratio $\phi_{CH_4}/\phi_{CH_3OH} \sim 0.14$ is expected from the competition of reactions 6, $2k_6 = 10^{10}$ M^{-1} s^{-1},[13] 7, and 8, $k_8 = 7.4 \times 10^5$ M^{-1} s^{-1}, under the assumption of steady-state concentrations of the intermediates $CH_3\cdot$ and $CuCH_3^{2+}$. This ratio is in good agreement with yields reported in Table I.

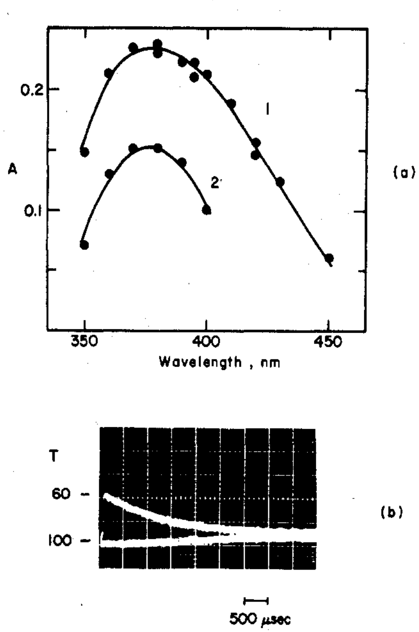

Figure 2. (a) Absorptions of transients generated in flash photolysis of $CuOCOCH_3^+$: (1) spectra obtained in solutions of $CuOCOCH_3^+$ ($[Cu^{2+}] = 10^{-3}$ M; $[CH_3CO_2^-] = 5 \times 10^{-3}$ M; $[CH_3CO_2H] = 5 \times 10^{-3}$ M); (2) spectra of the transient produced after successive irradiation of $Co(NH_3)_5OCOCH_3^{2+}$ in the presence of $Cu^{2+}(aq)$. See also Figure 1b. (b) Oscillographic trace for the decay process of the transient generated in flash photolysis of $CuOCOCH_3^+$: $\lambda_{excit} \geq 240$ nm; energy/flash 250 J.

A large accumulation of the products has a marked effect on the transient kinetics; see Figure 1b. The spectra of the new intermediate, obtained after four successive irradiations, has a maximum absorbance at 370–380 nm, Figure 2a, and disappears with a half-life time $t_{1/2} \sim 70$ μs. This transient is generated in reactions of cuprous ions with methyl radicals. In fact a species with almost identical properties was generated in flash photolysis of $Co(NH_3)_5OCOCH_3^{2+}$ in presence of cuprous ions. Irradiations of $Co(NH_3)_5OCOCH_3^{2+}$ (10^{-4} M) were studied in deaerated acidic (10^{-4} M $HClO_4$) solutions of cuprous ions (10^{-3} M $\geq [Cu^+] \geq 5 \times 10^{-5}$ M). A metastable species with an absorption maximum of 370 nm and a half-life of $t_{1/2} \sim 50$ μs was detected under the conditions indicated above.[14] Furthermore, the reactivity of methyl radicals toward cuprous ions was also investigated in the photochemical decomposition of $CuOCOCH_3^+$.[15] Indeed, redox processes, induced by irradiation of the charge-transfer bands, are expected to produce cuprous ions and acetate radicals.[16,17] These radicals decarboxylate through very fast reactions[18] and reaction of cuprous ions with methyl radicals might be observed in competition with radical–radical and radical–copper(II) reactions. A transient with $\lambda_{max} \sim 370$ nm, Figure 2a, was observed in flash photolyses ($\lambda_{excitation} \geq 240$ nm) of this species ($[Cu(ClO_4)_2] = 10^{-3}$ M; $[CH_3CO_2^-] + [CH_3CO_2H] = 10^{-2}$ M).[19] The decay process, Figure 2b, obeyed a second-order rate law with a first-order dependence on the concentration of transient and hydrogen ion ($k = (6.2 \pm 0.5) \times 10^7$ M^{-1} s^{-1}). Blanks, prepared without Cu(II), failed to produce transient absorptions.

Continuous way irradiations (λ_{exc} 254 nm; $I_0 = 8.0 \times 10^{-5}$ einstein/(L min)) produced large amounts of CH_4 and CO_2 compared with Cu(I) and C_2H_6. The distribution of products, Table Ib, shows that the dimerization of the methyl radicals, eq 20, cannot compete efficiently with their reduction. Equations 12–21 provide feasible channels for the observed photochemical decomposition of $CuOCOCH_3^{2+}$. In this regard, the chemical reactivity of the excited state, CT, might be described by eq 12 and/or 13. The species observed in flash photolysis is assigned as a product of the reaction of methyl radicals and copper(I), eq 15 and 17. Moreover, the low yield of Cu(I) compared with CO_2, Table Ib, suggests that processes 16 and 18 are not very efficient in this scheme, eq 12–21.

$$\mathrm{CuOCOCH_3^+} \xrightarrow[\phi]{h\nu} \mathrm{CT} \begin{array}{l} \nearrow [\mathrm{Cu^+,CH_3\cdot}] + \mathrm{CO_2} \qquad (12) \\ \searrow [\mathrm{Cu^+,O\dot{C}OCH_3}] \qquad (13) \end{array}$$

$$[\mathrm{Cu^+,O\dot{C}OCH_3}] \rightarrow \mathrm{CuOCOCH_3^+} \tag{14}$$

$$\rightarrow \mathrm{CuCH_3^+} + \mathrm{CO_2} \tag{15}$$

$$\rightarrow \mathrm{Cu_{aq}^+} + \mathrm{CH_3\cdot} + \mathrm{CO_2} \tag{16}$$

$$[\mathrm{Cu^+,CH_3\cdot}] \rightarrow \mathrm{CuCH_3^+} \tag{17}$$

$$\rightarrow \mathrm{Cu_{aq}^+} + \mathrm{CH_3\cdot} \tag{18}$$

$$\mathrm{CuCH_3^+} + \mathrm{H^+} \rightarrow \mathrm{Cu^{2+}} + \mathrm{CH_4} \tag{19}$$

$$\mathrm{CH_3\cdot} + \mathrm{CH_3\cdot} \rightarrow \mathrm{C_2H_6} \tag{20}$$

$$\mathrm{CH_3\cdot} + \mathrm{CuOCOCH_3^+} \rightarrow \mathrm{Cu^+} + \begin{array}{c} \mathrm{CH_3OH + CH_3CO_2H} \\ \text{and/or} \\ \mathrm{CH_3OCOCH_3} \end{array} \tag{21}$$

The results, described above, reveal some new and interesting features of the reactions between alkyl radicals and copper complexes. The fast formation of $CuCH_3^{2+}$, followed by its slow decay, shows that the formation of the alkyl–copper complex, eq 1, is not always the rate-determining step of the mechanism 1–4.[1b] The lifetime for the methylcopper(II) intermediate $CuCH_3^{2+}$ ($k = 7.4 \times 10^2$ s^{-1}) is, indeed, very large if it is compared with hydroxymethylcopper(II) ($CuCH_2OH^{2+}$; $k \geq 10^8$ s^{-1}, see ref 19) and too short if it is compared with $CuCH_2CO_2^+$ ($k \sim 2.8$ s^{-1}).[3] The opposite trend is observed with the formation rate constants ($k \sim 5 \times 10^5$ M^{-1} s^{-1} for $CuCH_3^{2+}$ and $k \sim 7 \times 10^8$ M^{-1} s^{-1} for $CuCH_2CO_2^+$). Such a variation of the reactivity suggests that both the decomposition and formation of these intermediates might be controlled by formation and dissociation of the carbon–metal bonds. In this regard, the stability of the bond in $CuCH_3^{2+}$ would be much lower than in the $CuCH_2CO_2^+$ species. Moreover, it seems that assignments of the metal centers as ions with a plus two or three oxidation state are meaningless in these kinds of alkyl–copper complexes if the metal–carbon bonds have a substantial degree of covalency. Indeed, the dissociation of $CuCH_3^+$ into Cu(I) ions and methanol cannot be reconciled with a tripositive ion forming a highly ionic carbon–metal bond.

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Registry No. $CuCH_3^{2+}$, 67049-31-4; $CuCH_3^+$, 67049-30-3; $Co(NH_3)_5OCOCH_3^{2+}$, 16632-78-3; $CuOCOCH_3^+$, 17203-87-1; Cu^{2+}, 15158-11-9.

References and Notes

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(14) Formation of such a species during the life of the flash requires a formation rate constant $k_{\mathrm{Cu(I)+CH_3\cdot}} \geq 10^9$ M^{-1} s^{-1} under the experimental conditions used in this work.

(15) The species $CuOCOCH_3^+$ is the only species present under the conditions used in this work. Equilibrium constants of the Cu(II)–$CH_3CO_2^-$ system were obtained from L. G. Sillen and A. E. Martell, "Stability Constants of Metal Ion Complexes", The Chemical Society, London, 1964.

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