consists of both intrinsic and solvational contributions, the latter being especially significant if there is charge creation or charge neutralization in the transition state. Thus, there would be considerable solvent electrostriction in the transition state for dissociation of $Cl^-$ from the unipositive *cis*-$Rh(bpy)_2Cl_2^+$ ion to produce the dipositive $Rh(bpy)_2Cl^{2+}$ pentacoordinate complex and a uninegative $Cl^-$. Such electrostriction is evidenced in an overall volume change of $-13.5$ cm$^3$ mol$^{-1}$ calculated for eq 1 from the partial molar volumes listed in Table IV. Furthermore, the overall volume change for the excited-state reaction (eq 2) would be significantly more negative, given that the $^3$LF state must have a volume significantly larger than does the ground state.[4,32] Thus, we conclude that the $\Delta V_p^{*}$ value measured for eq 2 is indeed consistent with the dissociative photosubstitution mechanism predicted for such d$^6$ complexes and demonstrated in the photoreactions of similar Rh(III) halo amine compounds.[33]

The volume of activation for nonradiative decay was calculated from the sum of $\Delta V_r^{*}$ and the pressure dependence of $\phi_n$ (as in eq 4). The result is $-1.5 \pm 0.2$ cm$^3$ mol$^{-1}$, having the same sign as that for photosubstitution but much smaller in magnitude. This is in accord with results for other amine complexes of rhodium(III)[4,34] and may indicate the parallel character of $k_p$ and a strong coupling contribution to $k_n$. This point will be discussed in greater detail elsewhere.[34]

**Acknowledgment.** This research was supported by grants to P.C.F. from the U.S. National Science Foundation (INT83-04030 and CHE84-19283) and to R.v.E. from the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie.

---

[32] DiBenedetto, J.; Ford, P. C. *Coord. Chem. Rev.* **1985**, *64*, 361.

[33] It is notable that the magnitude of $\Delta V_p^{*}$ is marginally greater for $Cl^-$ photoaquation from *cis*-$Rh(bpy)_2Cl_2^+$ than for the analogous reaction of $Rh(NH_3)_5Cl^{2+}$ ($-8.6 \pm 1.6$ cm$^3$ mol$^{-1}$)[4] despite the smaller contributions from solvent electrostriction expected for the aquation of $Cl^-$ from a +1 (rather than a +2) ion as evidenced by the smaller $\Delta\bar{V}$ for the former reaction.

[34] DiBenedetto, J.; Ford, P. C., manuscript in preparation.

---

Contribution from the Chemistry Department, Coal Research Center,
and Nuclear Research Center Negev, Ben Gurion University of the Negev, Beer-Sheva, Israel

# Effect of Nitrilotriacetate on the Mechanism of Reduction of Copper(II) Ions by α-Hydroxyalkyl Free Radicals via Complexes with Copper–Carbon Bonds as Intermediates. A Pulse-Radiolytic Study[†]

Mohamed Masarwa,[1a] Haim Cohen,*[1b] and Dan Meyerstein*[1a]

*Received February 12, 1986*

α-Hydroxyalkyl free radicals, $^{\bullet}CR_1R_2OH$, react with copper(II) nitrilotriacetate, $Cu(nta)^-(aq)$, in aqueous solutions to form the unstable intermediates $(nta)Cu^{III}{-}CR_1R_2OH^-(aq)$, or $(nta)Cu^{III}{-}CH_2O^{2-}(aq)$. These intermediates decompose by reducing a second $Cu^{II}(nta)^-(aq)$ complex, i.e. via the reaction $(nta)Cu^{III}{-}CR_1R_2OH^-(aq) + Cu^{II}(nta)^-(aq) \xrightarrow{H_2O} Cu^{I}(nta)^{2-}(aq) + Cu^{II}(nta)^-(aq) + CR_1R_2O + H_3O^+$. Unexpectedly, the intermediates do not decompose via first-order processes as expected. The spectrum of $(nta)Cu^{III}{-}CH_2OH^-(aq)$ is reported. The kinetics of reduction of $Co(NH_3)_6^{3+}$, $Ru(NH_3)_6^{3+}$, and $Fe(CN)_6^{3-}$ by the latter intermediate are reported.

## Introduction

The addition of copper ions was shown to affect the nature of the products in a variety of reactions involving aliphatic free radicals, including catalytic processes, in protic and aprotic media.[3] The results were interpreted as indicating that aliphatic free radicals, $^{\bullet}R$, react with copper(II) and copper(I) ions to form short-lived intermediates with copper–carbon bonds, e.g.

$$^{\bullet}R + Cu^{2+}(aq) \rightarrow Cu^{III}{-}R^{2+}(aq) \tag{1}$$

$$^{\bullet}R + Cu^{+}(aq) \rightarrow Cu^{II}{-}R^{+}(aq) \tag{2}$$

Indeed, reactions 1 and 2 were observed for a variety of free radicals and several complexes.[4-9] However, no such intermediates were observed[4] in the reactions

$$^{\bullet}CR_1R_2OH + Cu^{2+}(aq) \rightarrow Cu^{+}(aq) + CR_1R_2O + H_3O^{+} \tag{3}$$

It was however suggested that reaction 3 involves the formation of $Cu^{III}{-}CR_1R_2OH^{2+}(aq)$ as an intermediate but that its lifetime is too short to be observed. We decided to check wehther good σ-donating ligands, L, stabilize transients of the type $LCu^{III}{-}CR_1R_2OH$. Such an effect might be expected as such ligands stabilize complexes in higher oxidation states and therefore also decrease the free energy gain in reaction 3.

We wish to report that nitrilotriacetate, nta ($\equiv N(CH_2CO_2^-)_3$), indeed stabilizes such transients. Unexpectedly, the intermediates $(nta)Cu^{III}{-}CR_1R_2OH^{-2}$ do not decompose via a first-order process as expected but by reduction of another $Cu^{II}(nta)^-$ complex.

## Experimental Section

**Materials.** All chemicals used were of AR grade and were used without further treatment. All solutions were prepared with use of heat-distilled water, which was then passed through a Millipore setup, the final resistance being >10 MΩ. The $N_2O$ used was bubbled through two bottles containing $VSO_4$ in dilute $H_2SO_4$ over Zn analgam, followed by two washing bottles containing pure water. Acetate buffer was used when required to maintain constant pH during the experiments.

---

[†] Dedicated to Professor Leon Dorfman on the occasion of his retirement.

(1) (a) Chemistry Department and Coal Research Center. (b) Nuclear Research Center Negev and Coal Research Center.

(2) The exact nature of the transient complexes found in the reactions of $^{\bullet}CR_1R_2OH$ free radicals with $Cu^{II}(nta)^-(aq)$ is unclear. The formula $(nta)Cu^{III}{-}CR_1R_2OH^-(aq)$ is used throughout; however, the transients might be $(nta)Cu^{III}{-}CR_1R_2O^{2-}(aq)$ as well (see Results and Discussion).

(3) Kochi, J. K. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, Chapter II. Kochi, J. K. *Acc. Chem. Res.* **1974**, *7*, 351. Walling, C. *Ibid.* **1975**, *8*, 125.

(4) Freiberg, M.; Meyerstein, D. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1825. Freiberg, M.; Mulac, W. A.; Schmidt, K. H.; Meyerstein, D. *Ibid.* **1980**, *75*, 1838.

(5) Ferraudi, G. *Inorg. Chem.* **1978**, *17*, 2506. Geiger, D.; Ferraudi, G. *Inorg. Chim. Acta* **1985**, *101*, 197.

(6) Mulac, W. A.; Meyerstein, D. *J. Chem. Soc., Chem. Commun.* **1979**, 893.

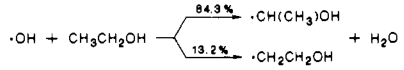
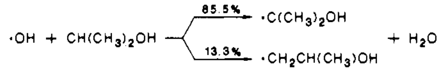
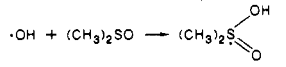
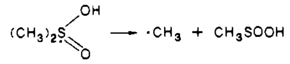
(7) Kirschenbaum, L. J.; Meyerstein, D. *Inorg. Chem.* **1980**, *19*, 1373.

(8) Das, S.; Johnson, G. R. A. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1779. Das, S.; Johnson, G. R. A.; Nazhat, N. B.; Saadalla-Nazhat, R. *Ibid.* **1984**, *80*, 2759.

(9) Buxton, G. V.; Green, J. C.; Sellers, R. M. *J. Chem. Soc., Dalton Trans.* **1976**, 2160. Buxton, G. V.; Green, J. C. *J. Chem. Soc., Chem. Commun.* **1976**, 158. Buxton, G. V.; Green, J. C. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 697. Buxton, G. V.; Sellers, R. M. *Coord. Chem. Rev.* **1977**, *27*, 195.

0020-1669/86/1325-4897$01.50/0

**Table I.** Reactions of the Primary Free Radicals[a]

| reacn no. | reacn | specific rate of reactn, $M^{-1}\ s^{-1}$ | ref |
|---|---|---|---|
| 5 | $e^-(aq) + N_2O \xrightarrow{H_2O} N_2 + {}^\bullet OH + OH^-(aq)$ | $8.7 \times 10^9$ | 13 |
| 6 | $e^-(aq) + Cu^{II}(nta) \rightarrow Cu^I(nta)^{2-}(aq)$ | $(1.0\text{–}3.3) \times 10^{10\,b}$ | 13 |
| 7 | ${}^\bullet OH + N(CH_2CO_2^-)_3 \rightarrow N(CH_2CO_2^-)_2({}^\bullet CHCO_2^-) + H_2O$ | $7.5 \times 10^{8\,c}$ | 12 |
| 8 | ${}^\bullet OH + Cu^{II}(nta)^-(aq) \rightarrow Cu^{III}(nta)(aq)$ | $2.6 \times 10^{9\,d}$ | 12 |
| 9 | ${}^\bullet OH + CH_3OH \rightarrow {}^\bullet CH_2OH + H_2O$ | $1.3 \times 10^9$ | 15 |
| 10 |  $\cdot OH + CH_3CH_2OH \rightarrow \{\xrightarrow{84.3\%} \cdot CH(CH_3)OH;\ \xrightarrow{13.2\%} \cdot CH_2CH_2OH\} + H_2O$ | $1.7 \times 10^9$ | 15 |
| 11 |  $\cdot OH + CH(CH_3)_2OH \rightarrow \{\xrightarrow{85.5\%} \cdot C(CH_3)_2OH;\ \xrightarrow{13.3\%} \cdot CH_2CH(CH_3)OH\} + H_2O$ | $2.3 \times 10^9$ | 16 |
| 12 | ${}^\bullet H + CH_3OH \rightarrow {}^\bullet CH_2OH + H_2$ | $2.0 \times 10^6$ | 16 |
| 13 | ${}^\bullet H + CH_3CH_2OH \rightarrow {}^\bullet CH(CH_3)OH + H_2$ | $4.0 \times 10^7$ | 16 |
| 14 | ${}^\bullet H + CH(CH_3)_2OH \rightarrow {}^\bullet C(CH_3)_2OH + H_2$ | $7.9 \times 10^7$ | 16 |
| 15 |  $\cdot OH + (CH_3)_2SO \rightarrow (CH_3)_2\dot{S}(OH)(=O)$ | $7.0 \times 10^9$ | 17 |
| 16 |  $(CH_3)_2\dot{S}(OH)(=O) \rightarrow \cdot CH_3 + CH_3SOOH$ | $1.5 \times 10^7$ | 17 |
| 17 | $e^-(aq) + Co(NH_3)_6^{3+} \rightarrow Co(NH_3)_6^{2+}$ | $9.0 \times 10^{10}$ | 13 |
| 18 | $e^-(aq) + Ru(NH_3)_6^{3+} \rightarrow Ru(NH_3)_6^{2+}$ | $7.9 \times 10^{10}$ | 13 |
| 19 | $e^-(aq) + Fe(CN)_6^{3-} \rightarrow Fe(CN)_6^{4-}$ | $3.0 \times 10^9$ | 13 |
| 20 | ${}^\bullet OH + Co(NH_3)_6^{3+} \rightarrow Co(NH_3)_5\dot{N}H_2 + H_2O$ | $<1.1 \times 10^8$ | 15 |
| 21 | ${}^\bullet OH + Ru(NH_3)_6^{3+} \rightarrow$ | slow, exact rate unknown | 18 |
| 22 | ${}^\bullet OH + Fe(CN)_6^{3-} \rightarrow$ | slow, exact rate unknown | 18 |
| 23 | ${}^\bullet H + Co(NH_3)_6^{3+} \rightarrow Co(NH_3)_6^{2+} + H_3O^+$ | $1.85 \times 10^6$ | 19 |
| 24 | ${}^\bullet H + Ru(NH_3)_6^{3+} \rightarrow Ru(NH_3)_6^{2+} + H_3O^+$ | $1.8 \times 10^6$ | 19 |
| 25 | ${}^\bullet H + Fe(CN)_6^{3-} \rightarrow Fe(CN)_6^{4-} + H_3O^+$ | $1.5 \times 10^9$ | 16 |

[a] The rates are literature values. No temperature is usually cited. Room temperature is assumed. [b] The rate of reaction of $Cu^{II}(nta)(aq)$ was not reported. The rate of reaction of $e^-(aq)$ with $Cu^{2+}(aq)$ is $3.3 \times 10^{10}\ M^{-1}\ s^{-1}$ and with $Cu^{II}(nta)_2^{4-}$ is $1.0 \times 10^{10}\ M^{-1}\ s^{-1}$.[14] [c] pH 5.0. [d] pH 9.0.

**Pulse Radiolysis.** Pulses (0.3–1.5 μs, 200 mA, 5 MeV of electrons) from the linear electron accelerator at the Hebrew University of Jerusalem were used. The dose per pulse was 300–3000 rd. The methods of solution preparation and analysis of the results were identical with those earlier described in detail.[10]

**Production of Free Radicals.** The radiolysis of water may be summed up by the equation

$$H_2O \xrightarrow{\gamma,\ e^-} e^-(aq),\ H,\ OH,\ H_2,\ H_2O_2,\ H_3O^+ \qquad (4)$$

The yield of the primary products is $G_{e^-(aq)} = G_{OH} = 2.65$, $G_H = 0.60$, $G_{H_2} = 0.45$, and $G_{H_2O_2} = 0.75$ in dilute aqueous solutions.[11] (Here $G$ is defined as the number of product molecules formed per 100 eV adsorbed in the solution). In concentrated solutions the yields of the free radicals are often somewhat larger whereas the yields of $H_2$ and $H_2O_2$ are somewhat smaller.[11]

In $N_2O$-saturated neutral solutions, $[N_2O] \approx 2.2 \times 10^{-2}$ M, containing $Cu^{II}(nta)^-(aq)$ and different organic solutes, the primary radicals, $e^-(aq)$, ${}^\bullet H$, and ${}^\bullet OH$, react with solutes according to the equations in Table I. The relative yields of the different products depend on the specific rates of reaction (Table I) and the concentrations of the solutes.

**Determination of Formaldehyde Yields.** The yield of formaldehyde was determined by the Schiff reagent *p*-rosaniline hydrochloride as described by Vogel.[20a]

## Results and Discussion

When $N_2O$-saturated neutral solutions containing $(1\text{–}100) \times 10^{-5}$ M $CuSO_4$ ($[Cu^{2+}]$), $1 \times 10^{-3}$ M nta, and 0.1 M $CH_3OH$ are irradiated, three consecutive processes are observed. Under these conditions all the primary free radicals are transformed into ${}^\bullet CH_2OH$ radicals (Table I). In the first process, the formation of a short-lived transient with an absorption band with $\lambda_{max} = 430 \pm 5$ nm and $\epsilon_{max} = 200 \pm 20\ M^{-1}\ cm^{-1}$ (Figure 1) is observed. In the second process the absorption due to the transient disappears. In the third process the formation of a colloidal precipitate is observed. The rate of the last process is sigmoidal, the apparent rate increasing upon consecutive pulsing.

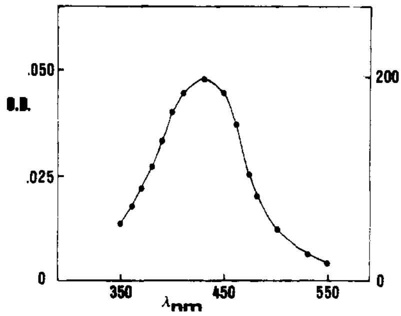


**Figure 1.** Spectrum of $(nta)Cu^{III}\text{–}CH_2OH^-(aq)$ 50 μs after the pulse. Solution composition: $5 \times 10^{-4}$ M $CuSO_4$, $1.5 \times 10^{-3}$ M nta, 0.1 M $CH_3OH$, $1 \times 10^{-2}$ M $CH_3CO_2Na$, pH 6.0, $N_2O$ saturated.

The first process observed obeys a pseudo-first-order rate law, the rate being proportional to the concentrations of $Cu^{II}(nta)^-(aq)$. The rate is independent of the concentrations of methanol and nta, as long as $[nta] > [Cu^{2+}(aq)]$, and the pH is in the range $5.0 \leq pH \leq 8.0$. The short-lived intermediate formed is clearly not $Cu^{III}(nta)(aq)$, as the latter has a totally different absorption spectrum.[12] Neither is the short-lived intermediate $Cu^I(nta)^{2-}(aq)$, as no absorption at 425 nm appears during the pulse when identical solutions (but He saturated) are irradiated. Under these conditions

---

(10) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1974**, *13*, 2434. Sorek, Y.; Cohen, H.; Mulac, W. A.; Schmidt, K. H.; Meyerstein, D. *Ibid.* **1983**, *22*, 3040.

(11) Matheson, M. S.; Dorfman, L. M. *Pulse Radiolysis*; MIT Press: Cambridge, MA, 1969; Chapter 6.

(12) Lati, J.; Meyterstein, D. *J. Chem. Soc., Dalton Trans.* **1974**, 2559.

(13) Anbar, M.; Bambeneck, M.; Ross, A. B. *Natl. Stand. Ref. Data Ser.* (*U.S. Natl. Bur. Stand.*) **1973**, *NSRDS-NBS 43*.

(14) Meyerstein, D.; Mulac, W. A. *Trans. Faraday Soc.* **1969**, *65*, 1818.

(15) Farhataziz; Ross, A. B. *Natl. Stand. Ref. Data Ser.* (*U.S. Natl. Bur. Stand.*) **1977**, *NSRDS*-NBS *59*.

(16) Anbar, M.; Farhataziz; Ross, A. B. *Natl. Stand. Ref. Ser.* (*U.S. Natl. Bur. Stand.*) **1975**, *NSRDS-NBS 51*.

(17) Veitwisch, D.; Janata, E.; Asmus, K. D. *J. Chem. Soc., Perkin Trans. 2* **1980**, 146.

(18) These specific rates have not been reported, but as solutions containing up to $1 \times 10^{-3}$ M of these solutes in the presence of 1 M $CH_3OH$ were used, these reactions clearly did not compete with reaction 12.

(19) Navon, G.; Meyerstein, D. *J. Phys. Chem.* **1970**, *74*, 4067.

reaction 6 replaces reaction 5 (Table I), and therefore $\mathrm{Cu^{I}(nta)^{2-}(aq)}$ is formed during the pulse. It is proposed that the short-lived transient observed is $\mathrm{(nta)Cu^{III}{-}CH_2OH^-(aq)}$ formed in reaction 26.

$$\mathrm{Cu^{II}(nta)^-(aq) + {}^{\bullet}CH_2OH \rightarrow (nta)Cu^{III}{-}CH_2OH^-} \quad (26)$$

The possibility that the transient is $\mathrm{(nta)Cu^{II}{-}CH_2OH^{2-}(aq)}$ formed via

$$\mathrm{Cu^{I}(nta)^{2-}(aq) + {}^{\bullet}CH_2OH \rightarrow (nta)Cu^{II}{-}CH_2OH^{2-}(aq)} \quad (27)$$

is ruled out by the following observations.

(a) The yield of the transient does not increase with $\mathrm{[Cu^{II}(nta)^-(aq)]}$ in the concentration range $(3\text{–}10) \times 10^{-4}$ M. The yield of $\mathrm{Cu^{I}(nta)^{2-}(aq)}$ formed in reaction 6, in competition with reaction 5, increases linearly with $\mathrm{[Cu^{II}(nta)^-(aq)]}$ in this concentration range.

(b) The rate of formation of the transient is independent of pulse intensity, whereas the concentration of $\mathrm{Cu^{I}(nta)^{2-}(aq)}$ naturally increases with the pulse intensity.

(c) When identical solutions (but He saturated) are irradiated, the formation of transients in the same spectral region is observed. However, their properties differ from those observed in the $\mathrm{N_2O}$-saturated solutions, as follows: (1) The rate of formation of the transients is considerably higher in the He-saturated solutions. The effect is largest for low concentrations of $\mathrm{Cu^{II}(nta)^-(aq)}$. This result indicates that in the He-saturated solutions reaction 27 competes with reaction 26 and that $k_{27} >> k_{26}$, in agreement with expectations.[4,5,9] (2) The lifetime of the transients in He-saturated solutions, a mixture of $\mathrm{(nta)Cu^{II}{-}CH_2OH^{2-}(aq)}$ and $\mathrm{(nta)Cu^{III}{-}CH_2OH^-(aq)}$, is considerably shorter than that of $\mathrm{(nta)Cu^{III}{-}CH_2OH^-(aq)}$ in $\mathrm{N_2O}$-saturated solutions. (3) No precipitate formation is observed after the decay of the transients in the He-saturated solutions. This result indicates that most of the $\mathrm{Cu^{I}(nta)^{2-}(aq)}$ formed in reaction 6 under these conditions is reoxidized by the $\mathrm{{}^{\bullet}CH_2OH}$ radicals.

These results indicate that in the $\mathrm{N_2O}$-saturated solutions $\mathrm{(nta)Cu^{III}{-}CH_2OH^-(aq)}$ is formed. In He-saturated solutions a mixture of $\mathrm{(nta)Cu^{III}{-}CH_2OH^-(aq)}$ and $\mathrm{(nta)Cu^{II}{-}CH_2OH^{2-}(aq)}$ is formed. The properties of the latter complex cannot be studied in detail since it is always formed in a mixture with $\mathrm{(nta)Cu^{III}{-}CH_2OH^-(aq)}$ and both transients have similar lifetimes and spectra.[20b]

The kinetics of decomposition of $\mathrm{(nta)Cu^{III}{-}CH_2OH^-(aq)}$ obey a pseudo-first-order rate law, the rate being proportional to the concentration of $\mathrm{Cu^{II}(nta)^-(aq)}$ and independent of the pulse intensity, the concentrations of methanol, and excess nta or $\mathrm{[H^+]}$ in the pH range $5.0 \leq \mathrm{pH} \leq 8.0$. These results indicate that the transient decomposes via

$$\mathrm{(nta)Cu^{III}{-}CH_2OH^-(aq) + Cu^{II}(nta)^-(aq) \rightarrow}$$
$$\mathrm{Cu^{II}(nta)^-(aq) + Cu^{I}(nta)^{2-}(aq) + CH_2O + H_3O^+} \quad (28)$$

$$k_{28} = (4.0 \pm 0.6) \times 10^5 \ \mathrm{M^{-1}\ s^{-1}}$$

The dependence of the rate of decomposition on $\mathrm{[Cu^{II}(nta)^-(aq)]}$ proves that the decomposition does not follow a first-order mechanism as expected nor does it follow a mechanism involving $\mathrm{{}^{\bullet}CH_2OH}$ radicals formed via homolytic cleavage of the copper–carbon bond. The formation of $\mathrm{Cu^{I}(nta)^{2-}(aq)}$ in reaction 28 is evident from the following step, in which $\mathrm{Cu_2O}$ or Cu[20c] appears as a precipitate.

The yield of formaldehyde formed in reaction 28 was found to be 3.6 ± 0.8 i.e. ca. 60% of the expected yield. This result is not surprising, as at least 15 pulses yielding $3 \times 10^{-4}$ M free radicals were required for the determination and under these conditions reaction 27 is expected to compete efficiently with reaction 26 (see above).

**Table II.** Specific Rates of Reduction by $\mathrm{(nta)Cu^{III}{-}CH_2OH^-(aq)}$ and $\mathrm{{}^{\bullet}CH_2OH}$[a]

| oxidant | reducing agent<br>$\mathrm{(nta)Cu^{III}{-}CH_2OH^-(aq)}$ | <br>$\mathrm{{}^{\bullet}CH_2OH}$ |
|---|---|---|
| $\mathrm{Cu^{II}(nta)^-(aq)}$ | $4.0 \times 10^5$ | |
| $\mathrm{Co(NH_3)_6^{3+}}$ | $3.8 \times 10^5$ | $1.4 \times 10^8$ [b] |
| $\mathrm{Ru(NH_3)_6^{3+}}$ | $1.8 \times 10^8$ | $4.1 \times 10^7$ [b] |
| $\mathrm{Fe(CN)_6^{3-}}$ | $1.9 \times 10^7$ | $4.2 \times 10^9$ [c] |

[a] Specific rates in $\mathrm{M^{-1}\ s^{-1}}$ with precision ±15% at room temperature. [b] At pH 5–6.[22] [c] Refernece 23.

**Table III.** Specific Rates of Formation and Decomposition of $\mathrm{(nta)Cu^{III}{-}R^-}$[a]

| $\mathrm{{}^{\bullet}R}$ | $k(\mathrm{{}^{\bullet}R + Cu^{II}(nta)^-(aq)})$ | $k(\mathrm{(nta)Cu^{III}{-}R^-(aq) + Cu^{II}(nta)(aq)})$ |
|---|---|---|
| $\mathrm{{}^{\bullet}CH_2OH}$ | $1.9 \times 10^8$ | $4.0 \times 10^5$ |
| $\mathrm{{}^{\bullet}CH(CH_3)OH}$ | $6.0 \times 10^7$ | $1.3 \times 10^6$ |
| $\mathrm{{}^{\bullet}C(CH_3)_2OH}$ | $2.2 \times 10^7$ | $1.5 \times 10^6$ |
| $\mathrm{{}^{\bullet}CH_3}$ | $3.5 \times 10^7$ | 10 $(\mathrm{s^{-1}})$[b] |

[a] Specific rates in $\mathrm{M^{-1}\ s^{-1}}$ with accuracy ±15% at room temperature. [b] First-order specific rate of decomposition. This transient seems not to react with $\mathrm{Cu^{II}(nta)^-(aq)}$. However, due to the small absorption coefficient, the kinetics could not be studied in detail.

The results thus indicate that $\mathrm{(nta)Cu^{III}{-}CH_2OH^-(aq)}$ is a powerful reducing agent capable of reducing a second $\mathrm{Cu^{II}(nta)^-(aq)}$ complex, though the radical does not reduce the copper center to which it is bound. In this respect the results resemble those earlier reported for some $\mathrm{(NH_3)_5Co^{III}{-}O_2CCH_2A^{\bullet-}}$ complexes[21] (where $\mathrm{A^{\bullet-}}$ denotes substituted pyridinyl free radicals). We checked whether the transient complex $\mathrm{(nta)Cu^{III}{-}CH_2OH^-(aq)}$ acts as a reducing agent also toward other oxidizing agents. The results indicate that indeed it reduces $\mathrm{Co(NH_3)_6^{3+}}$, $\mathrm{Ru(NH_3)_6^{3+}}$, and $\mathrm{Fe(CN)_6^{3-}}$. The rates of reaction (Table II) are independent of the concentration of $\mathrm{Cu^{II}(nta)^-(aq)}$, nta, and methanol. For comparison purposes Table II includes also the specific rates of reaction of the $\mathrm{{}^{\bullet}CH_2OH}$ free radicals with the same oxidants. The results clearly indicate that different factors affect the rates of reduction by these reducing agents. The mechanism of reduction of $\mathrm{Co(NH_3)_6^{3+}}$,[22,24,25] and probably $\mathrm{Ru(NH_3)_6^{3+}}$,[22] by $\mathrm{{}^{\bullet}CH_2OH}$ is complex and probably involves bond formation between the radical and the complex.[22,24,25] The specific rate for the outer-sphere reduction of $\mathrm{Co(NH_3)_6^{3+}}$ by $\mathrm{{}^{\bullet}CH_2OH}$ is $<1 \times 10^3\ \mathrm{M^{-1}\ s^{-1}}$.[25] Thus, $\mathrm{(nta)Cu^{III}{-}CH_2OH^-(aq)}$ reduces $\mathrm{Co(NH_3)_6^{3+}}$, $\mathrm{Ru(NH_3)_6^{3+}}$, and $\mathrm{Cu^{II}(nta)^-(aq)}$ faster than the outer-sphere reduction of these complexes by $\mathrm{{}^{\bullet}CH_2OH}$ radicals. The slower reduction of $\mathrm{Fe(CN)_6^{3-}}$ is probably due to the negative charge of $\mathrm{(nta)Cu^{III}{-}CH_2OH^-(aq)}$.

The kinetics of decomposition of $\mathrm{(nta)Cu^{III}{-}CH_2OH^-(aq)}$ at pH <5.0 are more complex. The decomposition reaction is split into two consecutive processes, the rates of which are not well-separated. The overall rate of decomposition becomes greater. We did not study these processes in detail as the study is limited to pH ≥3.5 due to the stability constant of $\mathrm{Cu^{II}(nta)^-(aq)}$ and the p$K_a$ of nta. The results suggest that the transient complex $\mathrm{(nta)Cu^{III}{-}CH_2OH^-(aq)}$ has a p$K_a$ in this pH region. One possibility is

$$\mathrm{(nta)Cu^{III}{-}CH_2OH^-(aq) \rightleftharpoons (nta)Cu^{III}{-}CH_2O^{2-}(aq) + H_3O^+} \quad (29)$$

---

(20) (a) Vogel, A. I. In *A Text Book of Practical Organic Chemistry*, 3rd ed.; Longmans: London, 1972; p 330. (b) Therefore, our studies on the properties of the $\mathrm{(nta)Cu^{III}R}$ complexes were limited to $\mathrm{[Cu^{II}(nta)^-(aq)]} \leq 10^{-3}$ M, as otherwise reaction 6 competes considerably with reaction 5. (c) The kinetics of formation of the precipitate were not studied in detail. The precipitate disappears when oxygen is introduced into the solution, indicating that is a low-valent form of copper. From the color of the precipitate we belive that it is $\mathrm{Cu_2O}$ and not copper metal, but as the yields are low, this point was not studied in detail.

(21) Cohen, H.; Gould, E. S.; Meyerstein, D.; Nutkovitch, M.; Radlowski, C. A. *Inorg. Chem.* **1983**, *22*, 1374.

(22) Cohen, H.; Meyerstein, D. *J. Chem. Soc., Dalton Trans.* **1974**, 2559.

(23) Barker, G. C.; Fowles, P.; Stringer, P. *Trans. Faraday Soc.* **1970**, *66*, 1809.

(24) Olson, K. R.; Hoffman, M. Z. *J. Chem. Soc., Chem. Commun.* **1974**, 238.

(25) Espenson, J. H.; Shimura, M.; Bakac, A. *Inorg. Chem.* **1982**, *21*, 2537.

in analogy with $pK_a = 4.65$ for (nta)$Co^{III}$–$CH_2OH^-$(aq).[26] If this suggestion is correct, then the correct description of the observed transient in the pH range 5–8 is (nta)$Cu^{III}$–$CH_2O^{2-}$(aq) and this formula should replace that of (nta)$Cu^{III}$–$CH_2OH^-$(aq) throughout.

Finally, we checked whether similar intermediates are formed by analogous free radicals. The results (Table III) point out that analogous intermediates are indeed formed in the reactions of $^\bullet CH(CH_3)OH$, $^\bullet C(CH_3)_2OH$, and $^\bullet CH_3$ free radicals with $Cu^{II}$(nta)$^-$(aq). The specific rates of reaction of $^\bullet CH(CH_3)OH$ and $^\bullet C(CH_3)_2OH$ with $Cu^{II}$(nta)$^-$(aq) are lower than those of $^\bullet CH_2OH$ in analogy with the specific rates of these radicals with $Cu^{2+}$(aq).[4] The absolute rates of reaction are also similar. On the other hand, the specific rate of reaction of $^\bullet CH_3$ with $Cu^{II}$(nta)$^-$(aq) is considerably higher than that with $Cu^{2+}$(aq).[5] This result is in accord with expectations as the nta ligand stabilizes the tervalent transient complex.

The transient complexes (nta)$Cu^{III}$–$CH(CH_3)OH^-$(aq) and (nta)$Cu^{III}$–$C(CH_3)_2OH^-$(aq) reduce $Cu^{II}$(nta)$^-$(aq) somewhat faster than (nta)$Cu^{III}$–$CH_2OH^-$(aq). This result is in accord with the redox potentials of the $^\bullet CH_2OH$, $^\bullet CH(CH_3)OH$, and $^\bullet C(CH_3)_2OH$ free radicals.[27] Due to the low rates of reaction of the last two free radicals with $Cu^{II}$(nta)$^-$ we were unable to determine the yield of $CH_3CHO$ and $(CH_3)_2CO$ in these systems.[28]

The transient complex (nta)$Cu^{III}$–$CH_3^-$(aq) decomposes in a process that seems to obey a first-order rate law with $k = 10 \pm 3$ s$^{-1}$. However, due to the low absorption coefficient of this transient we did not study its properties in detail.

**Acknowledgment.** This study was supported in part by a grant from the Planning and Granting Committee of the Council of Higher Education and the Israel Atomic Energy Commission.

**Registry No.** $Co(NH_3)_6^{3+}$, 14695-95-5; $Ru(NH_3)_6^{3+}$, 18943-33-4; $Fe(CN)_6^{3-}$, 13408-62-3; $^\bullet CH_2OH$, 2597-43-5; $^\bullet C(CH_3)_2OH$, 5131-95-3; $^\bullet CH_3$, 2229-07-4; $^\bullet CH(CH_3)OH$, 2348-46-1.

---

(26) Meyerstein, D.; Schwarz, H. A. submitted for publication *J. Am. Chem. Soc.*

(27) Endicott, J. F. In *Concepts of Inorganic Photochemistry*; Adamson, A. W., Fleischauer, R. D., Eds.; Wiley: New York, 1975; pp 90–92.

(28) Acetaldehyde and acetone are products of the reaction mixture. This is however no proof for the suggested mechanism as they might be formed in the competing reaction $2CR_1R_2OH \rightarrow CR_1R_2O + CHR_1R_2OH$.

---

Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

# Kinetics of the Iodine Monochloride Reaction with Iodide Measured by the Pulsed-Accelerated-Flow Method

Dale W. Margerum,* Peter N. Dickson, Julius C. Nagy, Krishan Kumar, Conrad P. Bowers, and Kimber D. Fogelman

*Received August 25, 1986*

The reaction $ICl + I^- \rightarrow I_2 + Cl^-$ is extremely rapid and is irreversible, so that it cannot be studied by either stopped-flow or relaxation methods. The kinetics are determined by measurement of the reactions of dichloroiodate(I) with iodide, $ICl_2^- + 2I^- \rightarrow I_3^- + 2Cl^-$, by the pulsed-accelerated-flow method, where the pseudo-first-order rate constants ($k_r$) range from 3800 to 70 000 s$^{-1}$. The rates are first order in $ICl_2^-$ concentration, and the $k_r$ values are proportional to the $I^-$ concentration, inversely proportional to the $Cl^-$ concentration, and independent of $H^+$ concentration (0.10–1.00 M). The resolved second-order rate constant for the reaction of ICl with $I^-$ equals 1.1 (±0.1) × 10$^9$ M$^{-1}$ s$^{-1}$ (25.0 °C, $\mu$ = 1.0).

## Introduction

Eigen and Kustin[1] determined the kinetics of halogen hydrolysis by the temperature-jump relaxation technique. This method also was used to determine rate constants of triiodide ion formation and dissociation.[2] However, the hydrolysis and redox kinetics of interhalogen species have not been examined. This is because most of the reactions are not reversible and therefore are not suitable for relaxation techniques. Furthermore, the reactions are too rapid to study by stopped-flow methods. The development of the pulsed-accelerated-flow (PAF) method[3-5] permits reactions to be studied that have half-lives as short as 4 μs. This makes it possible to study reactions that are 3 orders of magnitude faster than can be studied by stopped-flow methods, without the reversibility required by relaxation methods.

In recent studies of the reactions of chloramines with iodide ion, a $Cl^+$ transfer to give ICl as an intermediate is proposed.[6] It is therefore of special interest to know how rapidly iodide ion reacts with iodine monochloride. The reaction may be viewed as a redox process with a transfer of $I^+$ or as a substitution reaction around $I^+$, where $I^-$ replaces $Cl^-$. Much less attention has been paid to atom-transfer reactions than to electron-transfer reactions.[7] Knowledge of the kinetics and mechanisms of reactions between halide ions and interhalogens or halogens is limited. The PAF method can provide important new information in this area.

Iodine monochloride is not stable in aqueous solution, but dichloroiodate(I), $ICl_2^-$, forms readily and is very stable in solutions where the HCl concentration is 0.5 M or greater.[8] The equilibrium constant, $K_1$, for eq 1 is 6.0 × 10$^{-3}$ M.[9] The UV spectrum

$$ICl_2^- \rightleftarrows ICl + Cl^- \quad K_1 \qquad (1)$$

of $ICl_2^-$ has characteristic absorption bands at 224 nm ($\epsilon$ = 47 500 cm$^{-1}$ M$^{-1}$) and at 343 nm ($\epsilon$ = 243 cm$^{-1}$ M$^{-1}$).[8] A molar absorptivity value of 275 cm$^{-1}$ M$^{-1}$ has also been reported for the 343-nm band.[10] The equilibrium constant, $K_h$, for the hydrolysis

---

(1) Eigen, M.; Kustin, K. *J. Am. Chem. Soc.* **1962**, *84*, 1355–1361.

(2) Turner, D. H.; Flynn, G. W.; Sutin, N.; Beitz, J. V. *J. Am. Chem. Soc.* **1972**, *94*, 1554–1559.

(3) Jacobs, S. A.; Nemeth, M. T.; Kramer, G. W.; Ridley, T. Y.; Margerum, D. W. *Anal. Chem.* **1984**, *56*, 1058–1065.

(4) Nemeth, M. T.; Fogelman, K. D.; Ridley, T. Y.; Margerum, D. W. *Anal. Chem.*, in press.

(5) Nagy, J. C.; Dickson, P. N.; Margerum, D. W., to be submitted for publication.

(6) Kumar, K.; Day, R. A.; Margerum, D. W. *Inorg. Chem.*, in press.

(7) Taube, H. In *Mechanistic Aspects of Inorganic Reactions*; Rorabacher, D. B., Endicott, J. F., Eds.; ACS Symposium Series 198; American Chemical Society: Washington, DC, 1982; pp 151–179.

(8) Cason, D. L.; Neumann, H. M. *J. Am. Chem. Soc.* **1961**, *83*, 1822–1828.

(9) Faull, J. H. *J. Am. Chem. Soc.* **1934**, *56*, 522–528.

(10) Gillam, A. E.; Morton, R. A. *Proc. R. Soc. London, A* **1931**, *132*, 152–167.