**Figure 7.** Calculated distribution diagram for the species existing in solution for the system $Cu^{2+}$-Me$_2$pentaen with $[Cu^{2+}] = 10^{-3}$ mol dm$^{-3}$ and $[Me_2pentaen] = 10^{-3}$ mol dm$^{-3}$. Charges have been omitted.

nitrogens in the ligands, varying from log $K$ = 28.03 for [Cu$_2$-(Me$_2$pentaen)]$^{4+}$ to log $K$ = 41.17 for [Cu$_2$(Me$_2$nonaen)]$^{4+}$. These constants are higher than those found for their cyclic counterparts (see Figure 5). With Me$_2$hexaen, and the longer ligands, the formation of protonated binuclear complexes is also observed.

The first aspect to be remarked is that the smallest ligand of the series, Me$_2$pentaen, forms a binuclear complex, while its cyclic counterpart, [18]aneN$_6$, failed to form such a species.[26] If a symmetric coordination of Me$_2$pentaen is assumed, both copper(II) ions would be bound by just three nitrogens. As is well-known, two copper(II) sites with three nitrogens may readily incorporate an exogen ligand to complete the 4-coordination. In Figure 6, it can be seen that the hydroxylated species [Cu$_2$L(OH)]$^{3+}$ is the main species in solution from pH 7.5. The magnitude of the constant for the equilibrium [Cu$_2$L]$^{4+}$ + H$_2$O $\rightleftharpoons$ [Cu$_2$L(OH)]$^{3+}$ + H$^+$ (log $K$ = –6.03) suggests that the OH$^-$ is bridging both metal centers. For the complex [Cu(den)]$^{2+}$ (den = 1,4,7-triazaheptane) the constant for such a reaction is 3 orders of magnitude lower (log $K$ = –9.16).[30] Also, for the following terms of the series,

Me$_2$hexaen and Me$_2$heptaen, these constants are considerably lower (see Table II).

The increase in the values of the stability constants for the complexes [Cu$_2$L]$^{4+}$, together with the low values of their protonation constants, suggests that in these complexes all the nitrogens of the ligand are involved in the coordination to the metal ion. In fact, the stepwise constants related to the addition of the second copper(II) ion increase with the number of nitrogen donors in the ligand. For Me$_2$nonaen, in which 10 nitrogens are available for coordinating the copper(II) ions, the values of the first and second stepwise stability constants are similar enough to assume pentacoordination for both metal ions. The close $\Delta H°$ values for both coordination steps are also confirming this assumption.

In Figure 7 are shown the calculated distribution diagrams for the equilibrium species formed in the system copper(II)–Me$_2$heptaen for 1:1 and 2:1 metal–ligand ratios. It can be seen that for the 1:1 metal–ligand ratio the mononuclear species are almost the only species in solution, while for the 2:1 metal–ligand ratio the binuclear species largely predominate. The two longer ligands Me$_2$octaen and Me$_2$nonaen behave similarly.

For analysis of the macrocyclic effect, the metathetical reaction [Cu$_n$L$_{cy}$] + L$_{oc}$ $\rightleftharpoons$ [Cu$_n$L$_{oc}$] + L$_{cy}$ ($n$ = 1–2; cy = cyclic, oc = open chain) has to be considered.[15] This reaction presents negative log $K$ values just for the mononuclear complexes of the ligands with six nitrogen donors, [18]aneN$_6$ and Me$_2$pentaen. This greater stability of the macrocyclic complex is due to a larger entropic contribution, even though the enthalpy is slightly more favourable for the formation of the open-chain complex. For the following terms of these series, Me$_2$hexaen and [21]aneN$_7$, the enthalpy term for the formation of the macrocyclic complex decreases to such extent that the macrocyclic effect vanishes, although the entropic term favors the formation of the macrocyclic complex (Table III). For all the other terms of both series, positive log $K$ values are found for the metathetical reaction above mentioned, independent of the mono- or binuclear nature of the complexes formed. In the case of the binuclear complexes of the ligands Me$_2$nonaen and [30]aneN$_{10}$, both the enthalpic and entropic contributions favor the open-chain ligand complex. Currently we are extending these studies to other metal ions to elucidate the extent of this "antimacrocyclic" effect.

(30) Castro, I.; Faus, J.; Julve, M.; Lloret, F.; Verdaguer, M.; Khan, O.; Jeannin, S.; Jeannin, Y.; Vaisserman, J. *J. Chem. Soc., Dalton Trans.* **1990**, 2207.

---

# Mechanism of Oxidation of the 2-Hydroxycyclohexyl Radical to Cyclopentanecarbaldehyde by Copper Ions in Aqueous Solutions

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

Copper ions are known to catalyze the oxidation of cyclohexene by persulfate to yield cyclopentanecarbaldehyde. The mechanism suggested in the literature for this process involves the reaction of 2-hydroxycyclohexyl free radicals with Cu$^{2+}$(aq). In the present study the kinetics of reaction of these free radicals with copper ions were studied by the pulse-radiolysis technique. The results indicate that the mechanism of the catalytic process involves the following reactions: The reaction of the free radical with Cu$^+$(aq), and not with Cu$^{2+}$(aq), yields the transient complex 1-cuprio-2-hydroxycyclohexane(1+). This transient complex rearranges in a reaction that involves the ring contraction step to form 6-hydroxy-7$\lambda^2$-cuprabicyclo[3.2.0]heptane. The latter intermediate decomposes via heterolysis of one of the copper(II)–carbon σ bonds to form (1-cupriocyclopentyl)methanol(1+), which reacts with Cu$^{2+}$(aq) to form the final product, cyclopentanecarbaldehyde. The rates of the first three reactions in this sequence and the spectra of the first two intermediates are reported. The results thus point out the possibility to use the pulse-radiolysis technique to elucidate the mechanisms of complex catalytic processes.

Olefins are oxidized by persulfate ions, in aqueous solutions, to form a mixture of products. Thus, for example, the oxidation of cyclohexene yields a mixture of I–III.[2] It was suggested[2] that these products are formed via the reaction sequence

$$S_2O_8^{2-} \longrightarrow 2SO_4^{\bullet -} \tag{1}$$

$$\text{(2)}$$

$$\text{I} \tag{3}$$

$$\text{II} \quad \text{III} \tag{4}$$
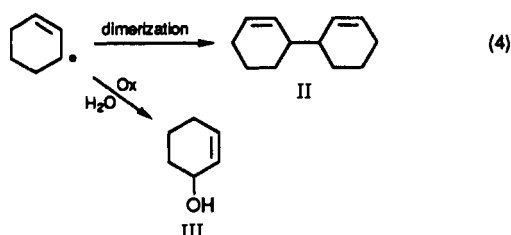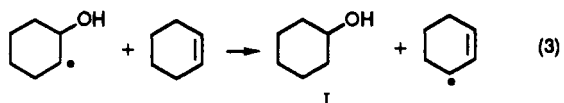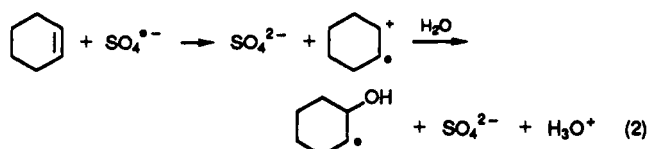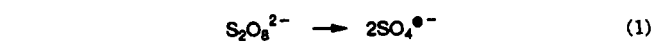
It was found that these oxidations are catalyzed by transition-metal cations, e.g. $Cu^{2+}(aq)$, $Fe^{2+}(aq)$, and $Ag^+(aq)$.[2] Furthermore, these cations affect the nature of the final products. Thus, when $Cu^{2+}(aq)$ ions are used as catalysts for the oxidation of cyclohexene, the final product is cyclopentanecarbaldehyde.[2]
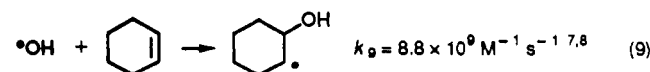
$$\text{(5)}$$
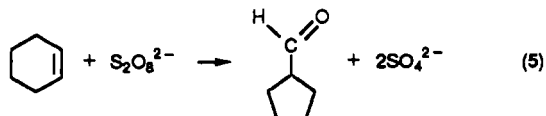
It was proposed[2] that the detailed mechanism of this process involves the following steps:

$$\text{(6)}$$

$$\text{(7)}$$

$$Cu^+(aq) + S_2O_8^{2-} \longrightarrow Cu^{2+}(aq) + SO_4^{2-} + SO_4^{\bullet -} \tag{8}$$
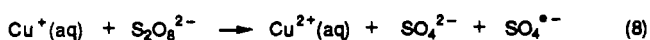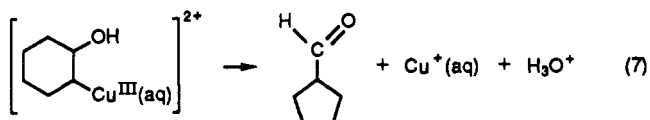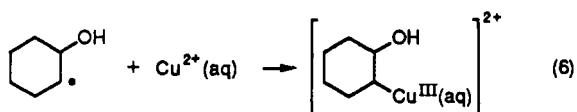
It was suggested[2] that the ring contraction step, reaction 7, proceeds in analogy to the Wagner–Meerwein rearrangement.[3] Similar mechanisms were proposed for the oxidation of cyclohexene by Tl(III),[4] Pb(IV),[5] and Hg(II),[6] which yield the same product.

It seemed of interest to study the detailed mechanism of reaction 7 as it probably consists of several steps and as the rates of such reactions have not been previously studied. As the 2-hydroxycyclohexyl free radical can be readily prepared via the reaction

$$k_9 = 8.8 \times 10^9 \ M^{-1} \ s^{-1} \ [7,8] \tag{9}$$

---

(1) (a) Chemistry Department, Ben-Gurion University of the Negev. (b) R. Bloch Coal Research Center, Ben-Gurion University of the Negev. (c) Nuclear Research Centre Negev.

(2) Arroldi, C.; Citero, A.; Miniski, F. *J. Chem. Soc., Perkin Trans. 2* **1983**, 531.

(3) Pine, S. H.; Hendrickson, H. B.; Cram, D. J.; Hammond, G. S. *Organic Chemistry*, 4th ed., Int. Stud. ed.; McGraw Hill: New York, 1981; pp 897–903.

(4) McKillop, A.; Hunt, J. P.; Kienzle, F.; Bigham, E.; Taylor, E. C. *J. Am. Chem. Soc.* **1973**, *95*, 3635.

(5) Rawlison, D. J.; Sosnovsky, G. *Synthesis* **1973**, 567.

(6) Arzanmanian, H.; Metzger, J. *Synthesis* **1971**, 527.

(7) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.

---

it seemed that the pulse-radiolysis technique would be best suited for this study. The results obtained point out that reaction 7 is not a step in the oxidation of the 2-hydroxycyclohexyl free radical to form cyclopentanecarbaldehyde. It is shown that the first reaction occurring is

$$\text{(10)}$$
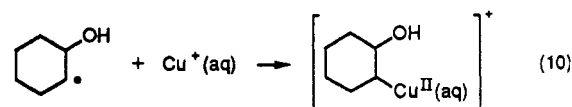
This reaction is followed by several steps leading to the final products.

## Experimental Section

**Materials.** All chemicals were of analytical grade and were used without further purification. All solutions were prepared with heat-distilled water, which was further purified by a Millipore setup, the final resistance being $>10$ M$\Omega$/cm. The N$_2$O used was bubbled through two gas washing bottles containing VSO$_4$ in dilute H$_2$SO$_4$ over Zn amalgam, followed by two washing bottles containing pure water. pH was adjusted by HClO$_4$ and/or NaOH. The cyclohexene, 98% supplied by Aldrich, was further purified by distillation. The fraction that is distilled at 83 °C was collected and stored over molecular sieves. The cyclohexene thus prepared was used within several days.

Solutions containing Cu$^+$(aq) were prepared via reaction 11.[9]

$$Cu^{2+}(aq) + Cr^{2+}(aq) \longrightarrow Cu^+(aq) + Cr^{III}(aq) \tag{11}$$
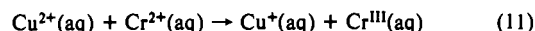
By the use of this reaction slightly acidic solutions containing $[Cu^+(aq)]/[Cu^{2+}(aq)] \leq 0.2$ can be easily prepared and kept for several hours.[9] Thus, all solutions containing Cu$^+$(aq) contained an equal concentration of Cr$^{III}$(aq). The latter complexes are known[10] to be unreactive toward aliphatic free radicals.

Cyclopentanecarbaldehyde was synthesized by oxidation of the corresponding alcohol, which was supplied by Aldrich. The oxidation was carried out according to a procedure described in the literature.[11] The product was identified by NMR, IR, GC, and MS methods.

**Irradiations.** Pulse-radiolysis experiments were carried out with the Varian 7715 linear electron accelerator of the Hebrew University of Jerusalem. The pulse duration was 0.1–1.5 $\mu$s with a 200-mA current of 5-Mev electrons. Irradiations were done in a 4-cm spectrosil cell by using three light passes. A 150-W Xenon arc produced the analyzing light. The experimental setup was identical with that described earlier in detail.[12] A N$_2$O-saturated solution containing 1 mM KSCN was used for dosimetry. The yield of (SCN)$_2^-$ was measured by taking $\epsilon_{475} = 7600$ M$^{-1}$ cm$^{-1}$ and assuming $G(\text{SCN})_2^-) = 6.0$.[12] The dose per pulse was set so that the initial free radical concentration was 2–20 $\mu$M. The values of the molar extinction coefficients calculated from dosimetry measurements have an error limit of at least 10% due to scatter in the repetition of the pulse intensity and due to uncertainties in $G$ values. Large doses of radiation for product analysis were delivered into bulbs (120-mL volume) filled with 100 mL of solution, saturated with N$_2$O, and sealed with a rubber septum. In this case the Fricke dosimeter was used for determining the total concentration of free radicals by taking $G(\text{Fe(III)}) = 15.6$ and $\epsilon_{302} = 2197$ M$^{-1}$ cm$^{-1}$.[12]

A $^{60}$Co source, Noratom, with a dose rate of 3.0 krad/min was used for low-dose-rate experiments and product analysis. Sample preparation and dosimetry were as described above for the high-integral-dose irradiations.

**Product Analysis. Yield of Cu$^+$(aq).** The d $\rightarrow \pi$ complex of Cu$^+$(aq) with cyclohexene has an absorption band with $\lambda_{max} = 300$ nm and $\epsilon_{max} = 630 \pm 60$ M$^{-1}$ cm$^{-1}$. The change in the concentration of Cu$^+$(aq) was therefore measured by recording the change in the absorption caused by the irradiation.

**Analysis of Organic Products.** Samples of 100-mL volume were irradiated either in the $^{60}$Co source or by the linac. Seven such samples were united and extracted with dichloromethane. The dichloromethane

---

(8) The product of reaction 9 was not identified in the past. However, as $\bullet$OH + C$_2$H$_4 \rightarrow \bullet$CH$_2$CH$_2$OH ($k = 4.4 \times 10^9$ M$^{-1}$ s$^{-1}$)[7] and as hydrogen abstraction reactions from unsubstituted hydrocarbons are considerably slower,[7] it is reasonable to assume that the 2-hydroxycyclohexyl free radical has been formed in this reaction. The observation of cyclopentanecarbaldehyde as the final product in the present study, see below, corroborates this assumption.

(9) Shaw, K.; Espenson, J. H. *Inorg. Chem.* **1968**, *7*, 1619.

(10) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1986**, *25*, 1506.

(11) Coney, E. J.; Suggs, W. *Tetrahedron Lett.* **1975**, *31*, 2647.

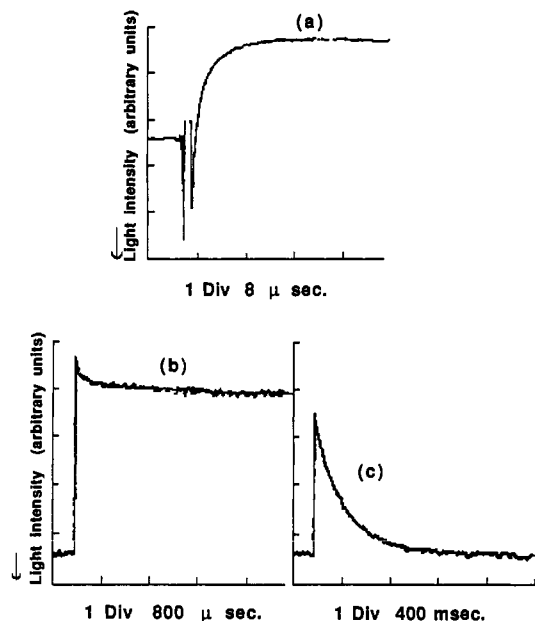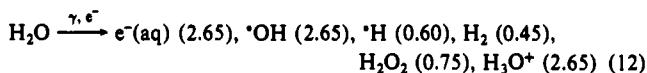(12) Matheson, M. S.; Dorfman, M. L. *Pulse Radiolysis*; MIT Press: Cambridge, MA, 1969.

**Figure 1.** Computer output showing the time dependence of the three processes observed after a short electron pulse is absorbed by the solution. Solution composition: $N_2O$ saturated, $[Cu^{2+}(aq)] = 7.5 \times 10^{-4}$ M, $[Cu^+(aq)] = 1 \times 10^{-4}$ M, $[CH_3CN] = 0.5$ M, and $[c\text{-}C_6H_{10}] = 0.15$ M at pH 5.0. Pulse intensity = 2500 rad/pulse, measured at 360 nm.

**Table I.** Reactions of the Primary Free Radicals with the Solutes Used in This Study

| reacn | $k$, $M^{-1}$ $s^{-1}$ | eq no. |
|---|---|---|
| $e^-(aq) + N_2O \xrightarrow{H_2O} {}^\bullet OH + OH^-(aq) + N_2$ | $8.7 \times 10^{9}$ [7] | 13 |
| $e^-(aq) + Cu^{2+}(aq) \rightarrow Cu^+(aq)$ | $3.0 \times 10^{10}$ [7] | 14 |
| $e^-(aq) + H_3O^+ \rightarrow {}^\bullet H + H_2O$ | $2.0 \times 10^{10}$ [7] | 15 |
| $e^-(aq) + CH_3CN \rightarrow a$ (at pH 7.2) | $3 \times 10^{7}$ [7] | 16 |
| $e^-(aq) + c\text{-}C_6H_{10} \rightarrow a$ (at pH 11) | $<2 \times 10^{6}$ [7] | 17 |
| ${}^\bullet OH + c\text{-}C_6H_{10} \rightarrow$ 2-hydroxycyclohexyl | $8.8 \times 10^{9}$ [7,8] | 9 |
| ${}^\bullet OH + CH_3CN \rightarrow {}^\bullet CH_2CN + H_2O$ | $(3.6-22) \times 10^{6}$ [7] | 18 |
| ${}^\bullet H + c\text{-}C_6H_{10} \rightarrow$ cyclohexyl | $3 \times 10^{9}$ [7,b] | 19 |
| ${}^\bullet H + CH_3CN \rightarrow a$ | $(8-220) \times 10^{4}$ [7] | 20 |
| ${}^\bullet OH + Cu^{2+}(aq) \rightarrow Cu^{III}(aq)$ | $3.1 \times 10^{8}$ [7] | 21 |
| ${}^\bullet H + Cu^{2+}(aq) \rightarrow Cu^+(aq) + H^+$ | $\leq 1 \times 10^{6}$ [13] | 22 |
| ${}^\bullet H + Cu^+(aq) \rightarrow Cu^{II}\text{-}H^+(aq)$ (followed by $Cu^{II}\text{-}H^+(aq) \rightarrow Cu^{2+}(aq) + H_2$) | $5 \times 10^9 < k <$ $2 \times 10^{10}$ [14] | 23 |
| ${}^\bullet OH + Cu^+(aq) \rightarrow Cu^{2+}(aq)$ | $2 \times 10^{10}$ [7] | 24 |
| $e^-(aq) + Cu^+(aq) \rightarrow Cu^0$ | $2.7 \times 10^{10}$ [7] | 25 |

*a* The product of this reaction has not been identified. *b* The product of this reaction has not been identified, but in analogy to reaction 9 one expects that the hydrogen atom adds to the double bond.

solution thus obtained was concentrated by vacuum evaporation to a known volume. The sample obtained was analyzed by GC and MS. Blanks of unirradiated samples and of unirradiated samples, to which known amounts of cyclopentanecarbaldehyde were added, were analyzed by the same techniques.

**Equipment.** The pH of solutions was determined with a Metrohm Model E 305B pH meter. Spectrophotometric measurements were carried out by using a Hewlett-Packard HP 8452 diode-array spectrophotometer. IR spectra were recorded with a Perkin-Elmer Model 781 spectrophotometer. NMR measurements were carried out by using a 200-MHz Bruker WP 200 (sy) spectrometer. GC analysis was carried out by using a Varian Model 3700 gas chromatograph equipped with a FID detector and a Poropak Q column with helium carrier gas. Mass spectrometric determinations were carried out by using a Balzers Model QMG 511 quadrupole mass spectrometer.

**Production of 2-Hydroxycyclohexyl Free Radicals.** The radiolysis of water may be summed up by the equation[12]

$$H_2O \xrightarrow{\gamma, e^-} e^-(aq)\ (2.65),\ {}^\bullet OH\ (2.65),\ {}^\bullet H\ (0.60),\ H_2\ (0.45),$$
$$H_2O_2\ (0.75),\ H_3O^+\ (2.65)\quad (12)$$

The numbers in parenthesis are $G$ values, which represent the number of molecules formed/100 eV of energy absorbed in the solution.[12] The precise values of the $G$'s are slightly dependent on solute concentrations. At high concentrations the yield of the free radicals increases and that of $H_2$ and $H_2O_2$ decreases.[12] The free radicals formed are homogeneously distributed in solution within less than 100 ns after the radiation is absorbed.

When nitrous oxide saturated solutions containing $(5-20) \times 10^{-4}$ M $CuSO_4$, $(0-4) \times 10^{-4}$ M $Cu^+(aq)$, $(0-4) \times 10^{-4}$ M $Cr^{III}(aq)$, $0.02-0.15$ M cyclohexene, and $0.15-0.65$ M $CH_3CN$ in the pH range 1–5.5 are irradiated, the reactions summed up in Table I have to be considered. From the table it is evident that reactions 16–18, 20, and 22–24 do not contribute to the processes observed. $CH_3CN$ was added to the reaction mixture in order to increase the cyclohexene solubility, at concentrations that do not affect the kinetics of reaction. It is evident from Table I that in the concentration ranges used all the primary free radicals are transformed into a mixture of 2-hydroxycyclohexyl and cyclohexyl free radicals. The relative yields of these free radicals depends on the pH, due to the competition between reactions 13 and 15. At pH $\geq$ 4 the ratio will be ca. 10:1 whereas at pH $\leq$ 1 it will be ca. 1:1.25.

**Results**

**Pulse Radiolysis.** When nitrous oxide saturated solutions containing $(5-20) \times 10^{-4}$ M $CuSO_4$, $(5-40) \times 10^{-5}$ M $Cu^+(aq)$, $(5-40) \times 10^{-5}$ M $Cr^{III}(aq)$, $0.02-0.15$ M cyclohexene, and $0.15-0.65$ M $CH_3CN$ in the pH range 1–5.5 are irradiated by a short electron pulse, three consecutive processes, well separated
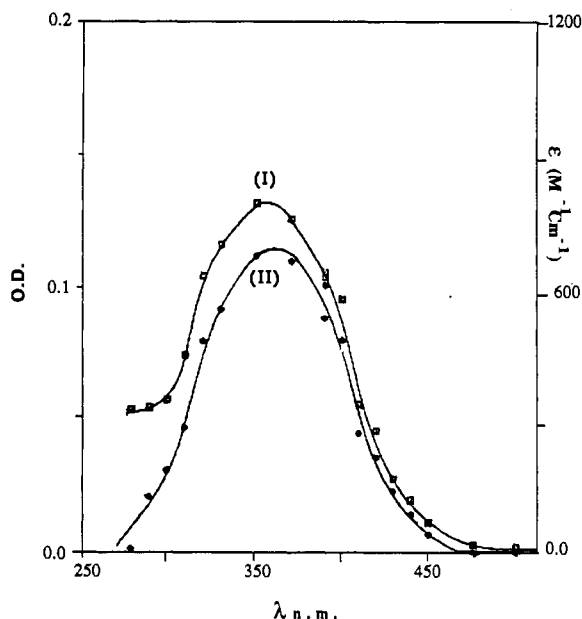


**Figure 2.** Spectra of the intermediates observed with experimental conditions as in Figure 1. The spectrum of the first intermediate was measured 10 $\mu$s after the pulse. The spectrum of the second intermediate was measured 1 ms after the pulse.

in time, are observed (Figure 1). Under these conditions all the hydroxyl free radicals are transformed into 2-hydroxycyclohexyl free radicals during the pulse (Table I).

In the first process the formation of a short-lived intermediate is observed. The spectrum of this intermediate is plotted in Figure 2. The spectrum of the intermediate in the region studied consists of one absorption band with $\lambda_{max} = 360 \pm 5$ nm and $\epsilon_{max} = 880 \pm 80$ $M^{-1}$ cm$^{-1}$ (the latter value is calculated from the calculated yield of hydroxyl radicals under the experimental conditions). The kinetics of formation of this intermediate obey a first-order rate law, the rate being proportional to the concentration of $Cu^+(aq)$. The rate is independent of the concentrations of all the other components of the solution, pulse intensity, and wavelength of observation. The kinetic results are summed up in Table II.

In the second process (Figure 1b), the first intermediate is transformed into a second intermediate. The spectrum of this intermediate is plotted in Figure 2. The spectrum of the second intermediate is similar to, though not identical with, that of the

(13) Freiberg, M.; Meyerstein, D. *J. Chem. Soc., Faraday Trans. 2* **1980**, *76*, 1825.

(14) Mulac, W. A.; Meyerstein, D. *Inorg. Chem.* **1982**, *21*, 1782.

**Table II.** Rates of the Processes Observed[a]

| pH | [Cu²⁺(aq)], M | [Cu⁺(aq)], M | rate, s⁻¹ [b] | | |
| --- | --- | --- | --- | --- | --- |
| | | | 1st process | 2nd process | 3rd process |
| 5.0 | $7.5 \times 10^{-4}$ | $5.0 \times 10^{-5}$ | $(2.0 \pm 0.2) \times 10^5$ | $3.5 \pm 0.4$ | $4.0 \pm 0.5$ |
| 5.0 | $7.5 \times 10^{-4}$ | $1.0 \times 10^5$ | $(3.4 \pm 0.4) \times 10^5$ | $3.5 \pm 0.4$ | $5.0 \pm 0.5$ |
| 5.0 | $7.5 \times 10^{-4}$ | $2.0 \times 10^{-4}$ | $(5.9 \pm 0.6) \times 10^5$ | $3.6 \pm 0.4$ | $4.0 \pm 0.5$ |
| 5.0 | $5.0 \times 10^{-4}$ | $1.0 \times 10^{-4}$ | $(3.2 \pm 0.4) \times 10^5$ | $3.3 \pm 0.4$ | $4.5 \pm 0.5$ |
| 5.0 | $2.0 \times 10^{-3}$ | $1.0 \times 10^{-4}$ | $(3.6 \pm 0.4) \times 10^5$ | $3.4 \pm 0.4$ | $5.0 \pm 0.5$ |
| 5.5 | $7.5 \times 10^{-4}$ | $1.0 \times 10^{-4}$ | $(3.5 \pm 0.4) \times 10^5$ | $3.5 \pm 0.4$ | $5.5 \pm 0.5$ |
| 3.0 | $7.5 \times 10^{-4}$ | $1.0 \times 10^{-4}$ | $(3.6 \pm 0.4) \times 10^5$ | $3.3 \pm 0.4$ | $5.1 \pm 0.5$ |
| 2.5 | $7.5 \times 10^{-4}$ | $1.0 \times 10^{-4}$ | $(3.2 \pm 0.4) \times 10^5$ | $3.7 \pm 0.4$ | $5.7 \pm 0.5$ |
| 2.0 | $7.5 \times 10^{-4}$ | $1.0 \times 10^{-4}$ | $(3.4 \pm 0.4) \times 10^5$ | $3.5 \pm 0.4$ | $6.5 \pm 0.5$ |
| 1.5 | $7.5 \times 10^{-4}$ | $1.0 \times 10^{-4}$ | $(3.3 \pm 0.4) \times 10^5$ | $3.3 \pm 0.4$ | $7.2 \pm 0.5$ |
| 1.0 | $7.5 \times 10^{-4}$ | $1.0 \times 10^{-4}$ | $(3.5 \pm 0.4) \times 10^5$ | $3.7 \pm 0.4$ | $12.5 \pm 0.5$ |
| 5.0 | $5.0 \times 10^{-4}$ | 0 | $(1.5 \pm 0.5) \times 10^{4c}$ | $3.5 \pm 0.4$ | $4.5 \pm 0.5$ |
| 5.0 | $1.0 \times 10^{-3}$ | 0 | $(2.5 \pm 0.5) \times 10^{4c}$ | $3.3 \pm 0.4$ | $4.5 \pm 0.5$ |
| 5.0 | $5.0 \times 10^{-3}$ | 0 | $(6.0 \pm 0.5) \times 10^{4c}$ | $3.7 \pm 0.4$ | $4.5 \pm 0.5$ |

[a] $N_2O$-saturated solutions containing 0.15 M cyclohexene and 0.5 M $CH_3CN$. The rates are independent of the concentrations of the latter two solutes, and the results of the study of these effects are therefore not shown. [b] All rates for the second process were multiplied by $10^{-3}$. [c] Result for first pulse to the sample.

first intermediate. The kinetics of the second process obey a first-order rate law. The rate is independent of the concentrations of all the components of the solution, pulse intensity, and wavelength of observation. The kinetic results are summed up in Table II.

In the third process (Figure 1c), the absorption due to the second intermediate disappears in a process that obeys a first-order rate law. The rate of this process increases somewhat when the pH is lowered and is independent of the concentrations of all other components of the solution, pulse intensity, and wavelength of observation. The kinetic results are summed up in Table II. The relative yields of intermediates I and II are pH independent.

Nitrous oxide saturated solutions containing $(1-5) \times 10^{-3}$ M $CuSO_4$, 0.15 M cyclohexene, and 0.15 M $CH_3CN$ at pH 5.0 were also irradiated. The rate of the first process observed under these conditions (Table II) is considerably lower than that observed in solutions containing $Cu^+(aq)$ ions; the rate in these solutions increased when consecutive pulses were delivered to the same solution. Furthermore, the absorption due to the transients in these experiments was considerably smaller than in the solutions containing $Cu^+(aq)$ ions, and it increased when consecutive pulses were delivered to the same solution.

**Product Analysis.** The yield (in $G$ values) of $Cu^+(aq)$ as determined by the absorption due to the d → π complex of $Cu^+(aq)$ with cyclohexene is $5 \pm 1$. The yield of cyclopentanecarbaldehyde as determined by GC is $4.5 \pm 1$.

When nitrous oxide saturated solutions containing $2 \times 10^{-3}$ M $CuSO_4$, $4 \times 10^{-4}$ M $Cu^+(aq)$, $4 \times 10^{-4}$ M $Cr^{III}(aq)$, 0.15 M cyclohexene, and 0.5 M $CH_3CN$ at pH 5.0 in $D_2O$, ca. 95%, were irradiated, mass spectrometric analysis (Table III) indicated that the product was labeled to a significant amount by two deuterium atoms.
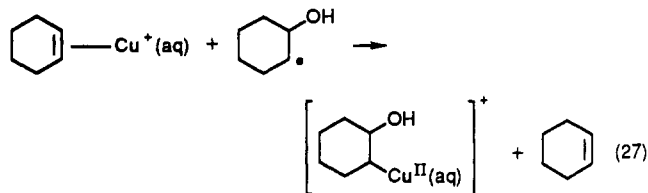
## Discussion

The spectra of $Cu^+(aq)$ in the presence of cyclohexene indicate that the equilibrium in reaction 26 is shifted to the right under

$$\text{(26)}$$
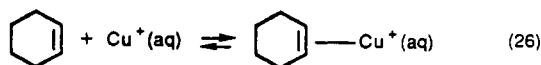
the experimental conditions, in analogy to other complexes of $Cu^+(aq)$ with olefins.[15] The results indicate that under the experimental conditions over 95% of the copper(I) ions are complexed by cyclohexene. Therefore, the latter complex is the reactant in all the reactions observed in which $Cu^+(aq)$ seems to be the reactant.

The results indicate that the first intermediate observed has been formed in reaction 27 and not in reaction 6 as has been

(15) (a) Ogura, T. *Inorg. Chem.* **1976**, *15*, 2301. (b) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; J. Wiley: New York, 1980; pp 809–810.

$$\text{(27)}$$

assumed.[2] This conclusion is based on the following observations: (1) The rate of the first process observed is proportional to the concentration of copper(I) and independent of the concentration of $Cu^{2+}(aq)$ (Table II). From the results $k_{27} = (2.6 \pm 0.2) \times 10^9$ $M^{-1}$ s⁻¹ is calculated. (2) The small absorption of the transients observed in the absence of $Cu^+(aq)$ is probably due, at least in part, to $Cu^+(aq)$ formed during the pulse via reaction 14 (Table I). This suggestion is based on the observation that this absorption increases upon repetitive pulses. From the results in Table II $k_6 \leq 1 \times 10^7$ $M^{-1}$ s⁻¹ is calculated.

These reaction rates indicate that in the catalytic system studied[2] the 2-hydroxycyclohexyl free radicals react with the copper(I) complex and not with $Cu^{2+}(aq)$, even if the steady-state concentration of the former is rather low.

Probably the cyclohexene ligand is not lost as suggested in eq 27, and therefore the correct description of the process might be as summed up in reaction 27a. (There is evidence in other systems

$$\text{(27a)}$$
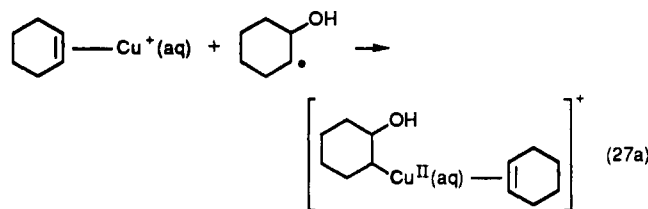
that when aliphatic radicals react with cuprous complexes with olefins, the latter remain bound to the intermediate that is formed.[16]) However, for brevity purposes it will be assumed in the following discussion that the intermediate observed is that formed in reaction 27; the same comment is true for all the intermediates discussed below that have a copper(II)–carbon bond.

The second process observed obeys a first-order rate law, the rate of reaction being independent of the concentrations of the solution components and the pulse intensity. These results suggest that the reaction observed is a rearrangement reaction of the first intermediate into a second intermediate. This conclusion is corroborated by the following observations: (1) The spectrum of the second intermediate though similar to that of the first intermediate (Figure 2) differs from it significantly. Thus, the ratios of the molar absorption coefficients of the two intermediates at 350 and 280 nm differ considerably. This result proves that the process observed is not a reaction of the first intermediate with a second species formed by the pulse with a significantly lower yield, e.g. with $H_2O_2$. (The rate of such a reaction would also depend on the pulse intensity.) (2) The relative absorption coefficients of the two intermediates at 360 nm are independent of the pH. This result indicates that the two intermediates are not formed in parallel by the reaction of copper(I) with the 2-hydroxycyclohexyl and the cyclohexyl free radicals.

When the nature of this rearrangement process is considered the following points have to be taken in account: (1) The spectrum of the second intermediate is similar to that of the first intermediate and to those of other intermediates with a copper(II)–carbon bond.[10,17,18] This observation suggests that the second intermediate also has a copper(II)–carbon σ bond. (2) The final

(16) Feldman, A.; Cohen, H.; Meyerstein, D. To be published.
(17) (a) Freiberg, M.; Mulac, W. A.; Schmidt, K. H.; Meyerstein, D. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1838. (b) Buxton, G. V.; Green, J. C. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 697. (c) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1987**, *26*, 2342. (d) Masarwa, M.; Cohen, H.; Meyerstein, D. *Isr. J. Chem.* **1990**, *30*, 361.
(18) Cohen, H.; Meyerstein, D. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 4157.

**Table III.** Mass Spectrometric Analysis of Cyclopentanecarbaldehyde[a]

| type of cyclopentanecarbaldehyde sample | ratio of masses 99/98 | ratio of masses 100/99 |
|---|---|---|
| synthetic sample | 0.060 ± 0.006 | 0.060 ± 0.010 |
| synthetic sample dissolved in $D_2O$ and dried | 0.80 ± 0.05 | 0.065 ± 0.010 |
| product obtained from a radiolysis experiment in $H_2O$ | 0.10 ± 0.05 | ≤0.1 |
| product obtained from a radiolysis experiment in $D_2O$ | 0.50 ± 0.05 | 0.44 ± 0.06 |

[a] The accuracy of the results is a function of signal to noise ratio, which depends on sample size.

product is cyclopentanecarbaldehyde. It is therefore reasonable to assume that the observed reaction involves the ring contraction step. (3) The lifetime of the second intermediate is considerably longer than that reported for any other intermediate with a copper(II)–carbon bond in aqueous solutions.[10,17,18] These considerations suggest that the rearrangement occurs via reaction 28 or via reaction 29. It is suggested that the second intermediate

(28)

(29)
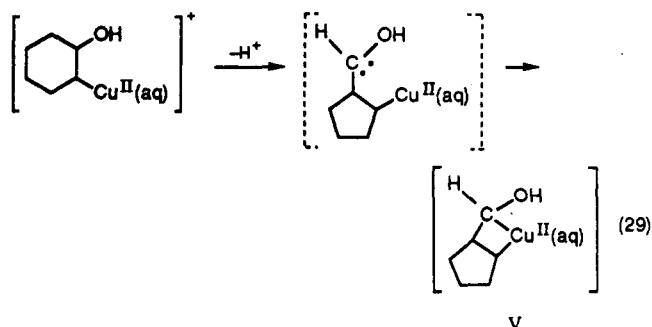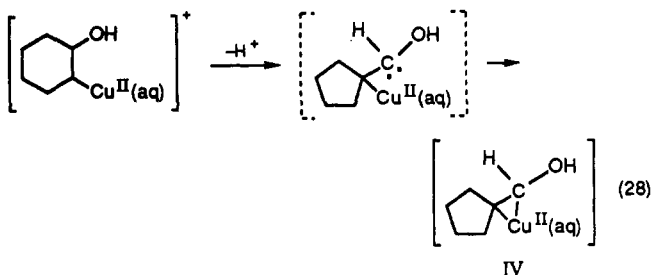
is either IV or V, as the alternative plausible intermediates VI, VII, and IX are expected to have a considerably shorter lifetime.[10,17,18] This is especially true for intermediate VII, which is the only one of the last three that leads to the observed final products; see below.

In the following sections these two possibilities are analyzed in detail. In the latter analysis it has to be taken into account that the decomposition of the second intermediate obeys a first-order rate law, the rate being independent of [$Cu^{2+}$(aq)] and [$Cu^+$(aq)]. However, this reaction is acid catalyzed. These results suggest that the rate-determining step in this process is the heterolysis of a copper(II)–carbon bond in agreement with analogous reactions.[10,17]

(I) Intermediate IV formed in reaction 28 might therefore decompose according to reaction 30 or 31. Intermediate VI formed

(30)
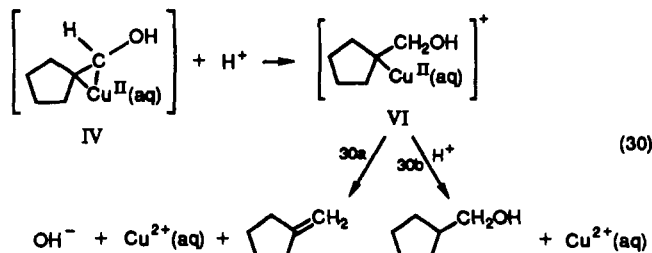
in the rate-determining step in reaction 30 might decompose in

**Scheme I**

k = (2.6 ± 0.2) x10⁹ M⁻¹s⁻¹

k = (3.5 ± 0.2) x10³ s⁻¹

k = 4.5 ± 0.5 s⁻¹ (rate at pH > 3 )
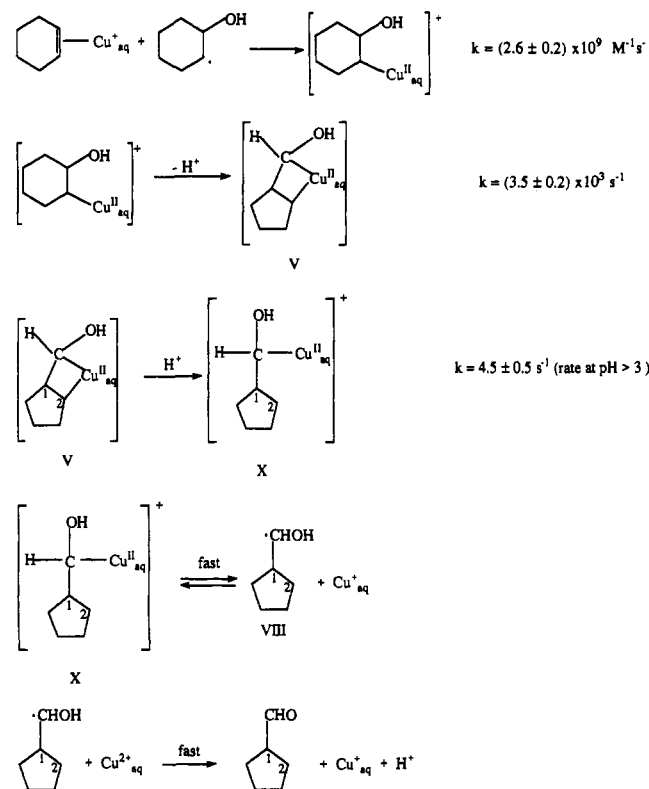
two routes: Reaction 30a, a β-hydroxyl elimination reaction is the more plausible route for the decomposition of intermediate VI, in analogy to other intermediates with a β-hydroxy substituent on an intermediate with a copper(II)–carbon bond.[17a,b,18] However, both reactions 30a and 30b yield the wrong final products. Intermediate VII formed in the rate-determining step of reaction 31 is expected to be in equilibrium with the free radical VIII.[17a]

(31)
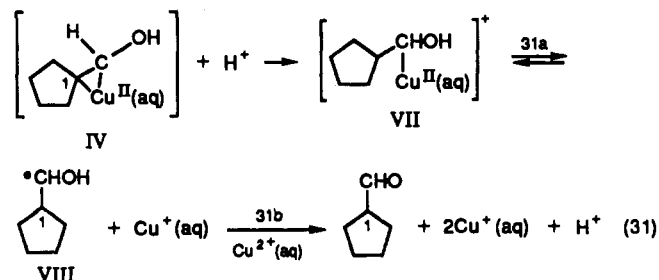
The equilibrium constant of reaction 31a is expected to be relatively small and the rate of achieving the equilibrium to be fast in analogy to other known complexes of α-hydroxy free radicals with $Cu^+$(aq).[17a] The free radical VIII is expected to reduce $Cu^{2+}$(aq) in a relatively fast reaction (reaction 31b) again in analogy with the known properties of α-hydroxy free radicals.[13] Thus, the final products expected to be formed according to a scheme involving reactions 28 and 31 are in accord with observations. According to this scheme only the hydrogen atom bound to the carbon 1 atom in the product originates from the solvent. Therefore, the results of the experiments carried out in $D_2O$ (Table III), which indicate that two of the hydrogen atoms in the product originate from the solvent, suggest that the product is not formed via this scheme. The results thus indicate that intermediate IV, which might be formed in reaction 28, is not the second intermediate observed in this study.

(II) Intermediate V formed in reaction 29 is expected to decompose via reaction 32 or 33, which are analogous to reactions 30 and 31 discussed above. Intermediate IX formed in the rate-determining step of reaction 32 is expected to decompose via heterolysis of the copper–carbon bond in analogy to the mechanism of decomposition of analogous complexes with copper(II)–carbon
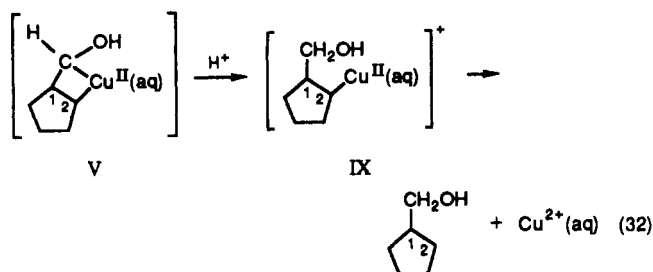
bonds.[10,17] Thus, reaction 32 does not lead to the formation of the final products observed. Alternatively intermediate V might decompose via reaction 33. Intermediate X formed in the latter
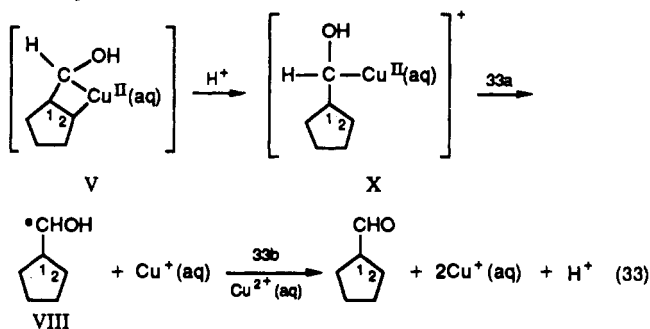


reaction is identical with intermediate VII formed in reaction 31. The decomposition of this intermediate is expected to yield the observed final products as discussed above. The only difference

between the final products of reaction 33 and reaction 31 is that according to reaction 33 one of the hydrogen atoms bound to carbon 2 originates from the solvent. As the hydrogen bound to carbon 1 is enolic, it exchanges rapidly with the solvent. Therefore, according to a mechanism involving reaction 33 it is predicted that when the experiments are carried out in $D_2O$ the product will be labeled by two deuterium atoms. This prediction is in full accord with the experimental results (Table III).

Thus, the results are in accord only with a scheme involving reaction 29 followed by reaction 33, and it is suggested that this is the mechanism of the processes observed.

## Concluding Remarks

The results obtained in this study indicate that the detailed mechanism of the oxidation of 2-hydroxycyclohexyl free radicals by copper ions in aqueous solutions involves the reactions summed up in Scheme I. These results point out that the mechanism of the catalytic oxidation of cyclohexene by persulfate in the presence of copper ions is totally different from that previously proposed.[2]

This study also points out the applicability of the pulse-radiolysis technique to the study of the detailed mechanisms of complex catalytic processes of this type.

---

# Thermodynamics of Chloro Complexation of Lanthanide(III) Ions in N,N-Dimethylformamide

Shin-ichi Ishiguro* and Ryouta Takahashi

The chloro complexation of a series of $Ln^{III}$ ions (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) has been studied by calorimetry in N,N-dimethylformamide (DMF) containing 0.2 mol $dm^{-3}$ $(C_2H_5)_4NClO_4$ as a constant ionic medium at 25 °C. The formation of $[LnCl]^{2+}$, $[LnCl_2]^{+}$, $[LnCl_3]$, and $[LnCl_4]^{-}$ complexes is revealed for all the metal systems except that of $La^{III}$. The $[LaCl_4^{-}]$ complex hardly forms. The large and positive enthalpy and entropy values show the favorable formation of inner-sphere chloro complexes for all the lanthanide(III) systems. The $\Delta H_1°$ and $\Delta S_1°$ values decrease with the atomic number Z for $La^{III}$, $Ce^{III}$, $Pr^{III}$, and $Nd^{III}$, while the values gradually increase with Z for $Sm^{III}$–$Er^{III}$. With respect to $Tm^{III}$, $Yb^{III}$, and $Lu^{III}$, the $\Delta H_1°$ and $\Delta S_1°$ values are particularly large and similar. The variation of $\Delta H_1°$ and $\Delta S_1°$ values along Z suggests that coordination energies and geometries of $Ln^{3+}$ solvates vary significantly with decreasing ionic radii. It is proposed that an equilibrium $[Ln(DMF)_8]^{3+} + DMF = [Ln(DMF)_9]^{3+}$ is established, which shifts to the right in the order La > Ce > Pr > Nd.

## Introduction

Much attention has been paid to the complexation of lanthanide(III) ions in aqueous solution, but somewhat less has been devoted to complexation in nonaqueous solution. Lanthanide(III) ions yield outer-sphere halogeno complexes in aqueous solution[1–5] but inner-sphere chloro complexes in dimethylacetamide (DMA),[6–8] methanol,[9] and propylene carbonate.[10] However, the

thermodynamic parameters thus far obtained in such nonaqueous solvents are not very reliable, and we believe that the thermodynamics of complexation of lanthanide(III) ions has not been established in nonaqueous solvents.

The coordination geometries of hydrated lanthanide(III) ions in solution have been explored by using various techniques such as X-ray and neutron diffraction and EXAFS.[11–19] It is widely

(1) Choppin, G. R.; Unrein, P. J. *J. Inorg. Nucl. Chem.* **1963**, *25*, 387.
(2) Peppard, D. F.; Mason, G. W.; Hucher, I. *J. Inorg. Nucl. Chem.* **1962**, *24*, 881.
(3) Khopkar, P. K.; Narayanankutty, P. *J. Inorg. Nucl. Chem.* **1971**, *33*, 495.
(4) Bansal, B. M. L.; Partil, S. K.; Shama, H. D. *J. Inorg. Nucl. Chem.* **1964**, *26*, 993.
(5) Breen, P. J.; Horrocks, W. D. *Inorg. Chem.* **1983**, *22*, 536.
(6) Vicentini, G.; Airoldi, C. *An. Acad. Brasil. Cienc.* **1970**, *42*, 3.
(7) Airoldi, C.; Vicentini, G. *An. Acad. Brasil. Cienc.* **1972**, *44*, 427.
(8) Volpe, P. L. O.; Chagas, A. P.; Airoldi, C. *J. Inorg. Nucl. Chem.* **1979**, *42*, 1321.
(9) Hamze, M.; Meullemeestre, J.; Schwing-Weil, M. J.; Vierling, F. *J. Less-Common Met.* **1986**, *118*, 153.

(10) Hamze, M.; Meullemeestre, J.; Vierling, F. *J. Less-Common Met.* **1989**, *146*, 75.
(11) Smith, L. S.; Wertz, D. L. *J. Am. Chem. Soc.* **1975**, *97*, 2365.
(12) Haubenschuss, A.; Spedding, F. H. *J. Chem. Phys.* **1979**, *70*, 2797, 3758; **1980**, *73*, 442.
(13) Narten, A. H.; Hahn, R. L. *J. Phys. Chem.* **1983**, *87*, 3193.
(14) Annis, B. K.; Hahn, R. L.; Narten, A. H. *J. Chem. Phys.* **1985**, *82*, 2086.
(15) Johansson, G.; Wakita, H. *Inorg. Chem.* **1985**, *24*, 3047.
(16) Yamaguchi, T.; Nomura, M.; Wakita, H.; Ohtaki, H. *J. Chem. Phys.* **1988**, *89*, 5153.
(17) Cossy, C.; Barnes, A. C.; Endaby, J. E.; Merbach, A. E. *J. Chem. Phys.* **1989**, *90*, 3254.
(18) Johansson, G. *Acta Chem. Scand.* **1989**, *43*, 307.