

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/243895196>

Mechanism of Reduction of 2,2-Dibromomethyl-1,3-propanediol by NiI-Tetraazamacrocyclic Complexes in Aqueous Solution— A Pulse Radiolysis and Electrochemical Study

ARTICLE *in* BERICHTE DER DEUTSCHEN CHEMISCHEN GESELLSCHAFT · NOVEMBER 2003

Impact Factor: 2.94 · DOI: 10.1002/ejic.200300114

CITATIONS

3

READS

6

7 AUTHORS, INCLUDING:



Israel Zilbermann

Ben-Gurion University of the Negev

66 PUBLICATIONS 773 CITATIONS

SEE PROFILE



Eric Maimon

Ben-Gurion University of the Negev

42 PUBLICATIONS 240 CITATIONS

SEE PROFILE



Haim Cohen

ariel university

219 PUBLICATIONS 2,600 CITATIONS

SEE PROFILE



Dan Meyerstein

Ariel University

350 PUBLICATIONS 5,073 CITATIONS

SEE PROFILE

Mechanism of Reduction of 2,2-Dibromomethyl-1,3-propanediol by Ni^I-Tetraazamacrocyclic Complexes in Aqueous Solution – A Pulse Radiolysis and Electrochemical Study

Elisabetha Shandalov,^[a] Israel Zilbermann,^[a,b] Eric Maimon,^[a,b] Yeoshua Nahmani,^[a,b] Haim Cohen,^[a,b] Eilon Adar,^[c] and Dan Meyerstein^{*[a,d]}

Keywords: Halogenated compounds / Pulse radiolysis / Reduction / Electrochemistry / Macrocycles

The reduction, catalytic reduction and the electrocatalytic reduction of halo-organic compounds are of major interest due to their role as pollutants. The mechanism and kinetics of reduction of 2,2-dibromomethyl-1,3-propanediol by several Ni^I tetraazamacrocyclic complexes, (Ni^ILⁱ)⁺ (i = 1–4), in aqueous solutions to yield Br[−] and the non-halogenated compound was studied using the pulse radiolysis technique. The rate constants $k = 5.3 \times 10^8$, 1.6×10^7 , 6.0×10^5 and $3.5 \times$

$10^4 \text{ M}^{-1}\text{s}^{-1}$ for L¹, L², L³ and L⁴ respectively, of the reactions (Ni^ILⁱ)⁺ + RBr → (Ni^{II}Lⁱ)²⁺ + Br[−] + R[•] increase with the free-energy gain in the reaction. All these complexes are good electrocatalysts for the reduction of this substrate. The mechanisms of the reductions are discussed.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003)

Introduction

Recently, the underground water of many sites all over the world has become heavily contaminated by halogenated organic compounds.^[1,2] Halogenated hydrocarbons such as halogenated methanes and ethanes are mainly used as solvents and are produced on a scale of 10^6 tons per year.^[3] Release of these hazardous compounds into the environment by leakage from industrial effluents causes ecological damage to the subsurface water reservoirs. Thus, the reduction, catalytic reduction and the electrocatalytic reduction of halo-organic compounds is of major interest for the removal of such compounds either from the raw effluents or for remediation of contaminated water. The kinetics and mechanisms of the reactions of nickel(II) macrocyclic complexes with alkyl halides have been investigated.^[4,5] Moreover these complexes have attracted considerable attention because they enable the electrocatalytic reduction of alkyl halides.^[6,7] Ni^{II}Lⁱ complexes, with macrocyclic ligands, are reduced reversibly to relatively stable nickel(I) species in

aqueous solution.^[8] The redox potentials and lifetimes of the Ni^IL complexes are affected mainly by three factors: 1) substitution on the macrocyclic ring (especially on the nitrogens), 2) ring size, and 3) saturation of the macrocyclic ring. Thermodynamic and/or kinetic stabilization of the monovalent nickel complexes is achieved by N-alkylation of the macrocyclic ligands.^[8,9]

It seemed of interest to study the effect of the redox potential, and plausibly of steric hindrance, of the nickel complexes on the rate of dehalogenation and on the detailed mechanism of the process. In this framework it was decided to study the reduction of 2,2-dibromomethyl-1,3-propanediol (as a representative contaminant found in the polluted groundwater in the Beer-Sheva region of Israel) by (Ni^ILⁱ)⁺ in aqueous solution. The tetraazamacrocyclic ligands Lⁱ (i = 1–4) were chosen as they affect both the redox potential of the central cation and impose different steric strains on the complex and on the approach of the substrate to the central nickel cation.

Results and Discussion

Pulse-Radiolysis Studies

He-saturated aqueous solutions containing 0.1 M HCOONa, 2×10^{-4} – 1×10^{-3} M (Ni^{II}Lⁱ)²⁺ and 1×10^{-4} to 2×10^{-3} M (CH₂Br)₂C(CH₂OH)₂, at pH 10.0 ± 0.3 , were irradiated by a short electron pulse from the linear

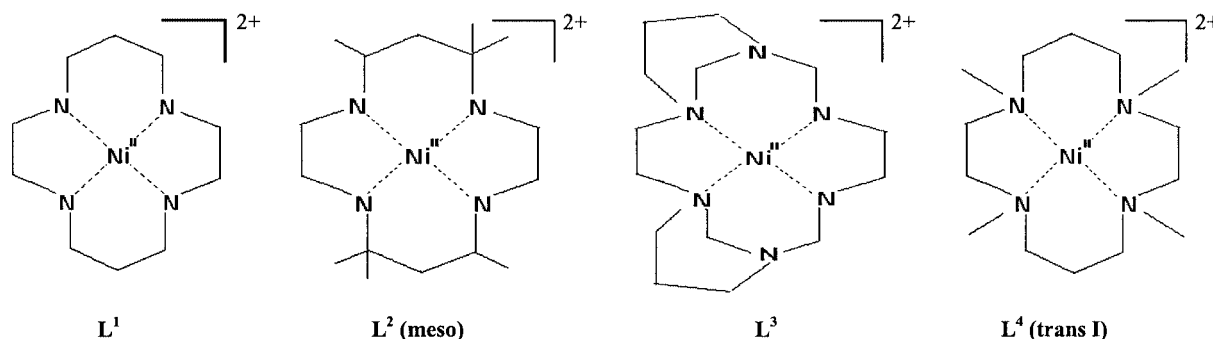
^[a] Chemistry Department, Ben-Gurion Univ. of the Negev, Beer-Sheva, Israel

E-mail: danmeyer@bgumail.bgu.ac.il

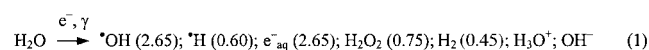
^[b] Nuclear Research Centre Negev, Beer-Sheva, Israel

^[c] Department of Environmental Hydrology and Microbiology, Institute for Water Sciences and Technologies – The J. B. Institutes for Desert Research, Ben-Gurion Univ. of the Negev, Beer-Sheva, Israel

^[d] Department of Biological Chemistry, College of Judea and Samaria, Ariel, Israel

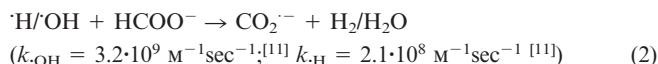


accelerator. When ionizing radiation is absorbed by a dilute aqueous solution the following initial products are formed:^[10]



Where the G values are given in parentheses (G values are defined as the number of molecules of each product per 100 eV of radiation absorbed by the solution).^[10]

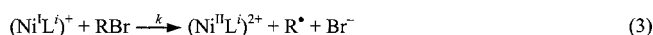
In the presence of formate (HCOO^-), both H^\cdot and $\cdot\text{OH}$, are scavenged by HCOO^- to generate the $\text{CO}_2^{\cdot-}$ radical.



The $\text{CO}_2^{\cdot-}$ radical generated and the hydrated electron, e_{aq}^- , are powerful single-electron reducing agents, $E^0 = -1.90 \text{ V}^{[12,13]}$ and $E^0 = -2.87 \text{ V}^{[11]}$ vs. NHE respectively. $\text{CO}_2^{\cdot-}$ is an inner-sphere reducing agent^[14] due to the fact that it is bent and the product, CO_2 , is linear.

The $\text{CO}_2^{\cdot-}$ radical and e_{aq}^- react rapidly with $(\text{Ni}^{\text{II}}\text{L})^{2+}$ to produce $(\text{Ni}^{\text{I}}\text{L})^+$ ^[8,15] which, in turn, reacts with the organic substrate in the next step. A typical experimental result is shown in Figure 1.

These results indicate that reactions (3) obey pseudo-first order rate laws. The rates of the dehalogenation reactions depend linearly on the $(\text{CH}_2\text{Br})_2\text{C}(\text{CH}_2\text{OH})_2$ concentration, Figure 2; the rate constants (k) derived from the slopes of the lines are summed up in Table 1.



Thus the results are in agreement with the suggestion that the reactions observed are reactions (3).

When the radical yield of reaction (3) is relatively low, i.e. when low pulse intensities are applied, and in the presence of a relatively high concentration of $(\text{Ni}^{\text{II}}\text{L})^{2+}$, the formation of a second intermediate is observed (Figure 3). It is proposed that this intermediate is $\text{L}^1\text{Ni}^{\text{III}}\text{-R}$, which is formed by

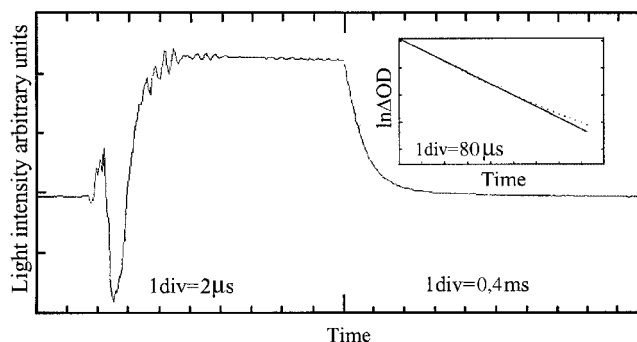
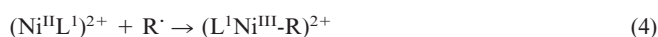


Figure 1. Decrease of the absorbance (at 380 nm) due to the reaction of $(\text{Ni}^{\text{I}}\text{L}^2)^+$ with $(\text{CH}_2\text{Br})_2\text{C}(\text{CH}_2\text{OH})_2$ and first order fit of the data (insert); solution composition: $1 \times 10^{-3} \text{ M}$ $(\text{Ni}^{\text{II}}\text{L}^2)^{2+}$, 0.1 M HCOONa and $3 \times 10^{-4} \text{ M}$ $(\text{CH}_2\text{Br})_2\text{C}(\text{CH}_2\text{OH})_2$ at $\text{pH } 10.0 \pm 0.3$, He sat, pulse intensity $(17.2 \pm 3.4) \text{ Gy/pulse}$

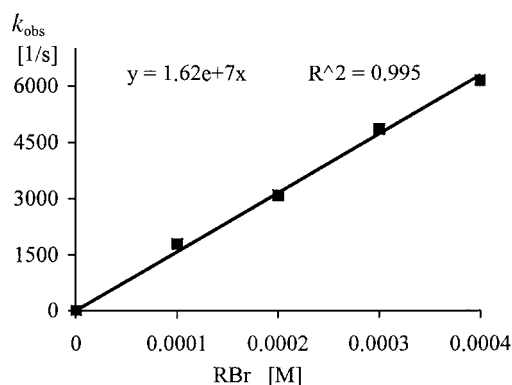


Figure 2. Dependence of k_{obs} on $[(\text{CH}_2\text{Br})_2\text{C}(\text{CH}_2\text{OH})_2]$, for the reaction of $(\text{Ni}^{\text{I}}\text{L}^2)^+$ with $(\text{CH}_2\text{Br})_2\text{C}(\text{CH}_2\text{OH})_2$

Table 1. Rate constants of the debromination reactions by the different nickel complexes

L^i	$E_{1/2}^0 \text{ Ni}^{2+/+} [\text{V}]$	$k [\text{M}^{-1}\text{s}^{-1}]$
L^1	-1.58	$(5.3 \pm 0.8) \times 10^8$
L^2	-1.42	$(1.6 \pm 0.2) \times 10^7$
L^3	-1.25	$(6.0 \pm 0.9) \times 10^5$
L^4	-1.15	$(3.5 \pm 0.5) \times 10^4$

This suggestion is supported by the observation that the absorbance due to the second intermediate increases with

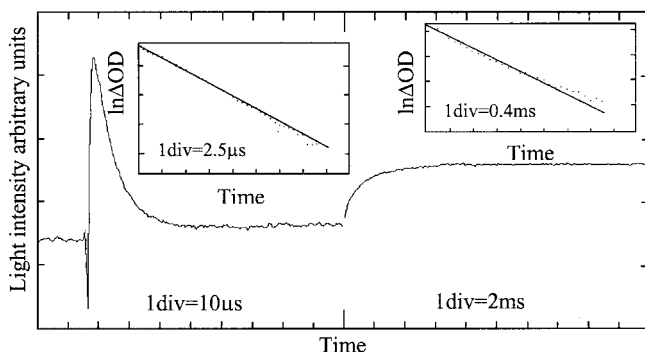
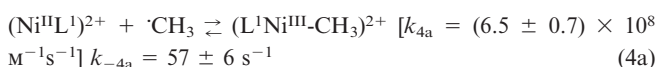


Figure 3. Decay of the absorption (at 370 nm) due to the reaction of (Ni^IL)⁺ with (CH₂Br)₂C(CH₂OH)₂ followed by increase of the absorption due to the formation of (L^INi^{III}R)²⁺; solution composition: 1 × 10^{−3} M (Ni^{II}L)²⁺, 0.1 M HCOONa and 4 × 10^{−4} M (CH₂Br)₂C(CH₂OH)₂, pH 10.0 ± 0.3, He sat, pulse intensity (5.9 ± 1.2) Gy/pulse

concentration of (Ni^{II}L)²⁺, as reaction (4) has to compete with reaction (5)



The analogous reaction



is well documented in the literature.^[16,17]

This competition also explains why this intermediate is not observed at high pulse intensities. The lifetime of (L^INi^{III}-R)²⁺ is considerably longer than 40 sec, in agreement with the reported lifetime of (L^INi^{III}-CH₃)²⁺.^[16]

The formation of the second intermediate is not observed for the other complexes studied, probably due to steric hindrance, which slows down reactions analogous to reaction (4), and to the fact that *k*₃ is slower for these complexes.

It is of interest to note that a plot of log *k* vs. *E*^o(Ni^{II}/L) yields a straight line (Figure 4). As the self-exchange rate for the Ni^{II}/L couples is relatively slow,^[8,15] and as the self exchange for the RBr/RBr^{•−} couple is probably not high and the free energy gain in the outer sphere reduction



is also not high, due to the instability of RBr^{•−}, it is proposed that reaction (3) probably proceeds via an inner-

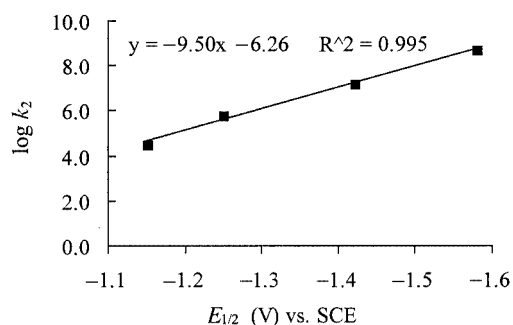


Figure 4. Dependence of log *k*₂ on *E*_{1/2} of the complexes

sphere mechanism. However, the straight line observed in Figure 4 suggests that steric hindrance does not slow down reaction (3) considerably.

Yield of Bromide

He-saturated aqueous solutions containing 0.1 M HCOONa, 5 × 10^{−4} M (Ni^{II}L)²⁺ and 2.5 × 10^{−4} to 7 × 10^{−3} M (CH₂Br)₂C(CH₂OH)₂, at pH 10, were irradiated in the ⁶⁰Co γ source with a dose rate of 4 Gy/min to an overall dose of 720 Gy. The yields of bromide obtained by the γ irradiation in the ⁶⁰Co source are summed up in Table 2.

Table 2. Bromide yield as a function of (CH₂Br)₂C(CH₂OH)₂ concentration; solution composition: 0.1 M HCOONa, 5 × 10^{−4} M (Ni^{II}L)²⁺ and 2.5 × 10^{−4} to 7 × 10^{−3} M (CH₂Br)₂C(CH₂OH)₂, pH 10.0 ± 0.3, He sat., dose 720 Gy at 4 Gy/min; experimental error: ±20%

[RBr] (M)	[Br [−]] (M)	G (Br [−])
2.5 × 10 ^{−4}	4.9 × 10 ^{−4}	> 7.8
5.0 × 10 ^{−4}	9.8 × 10 ^{−4}	> 15
1.0 × 10 ^{−3}	2.0 × 10 ^{−3}	> 32
3.0 × 10 ^{−3}	2.2 × 10 ^{−3}	35
5.0 × 10 ^{−3}	2.6 × 10 ^{−3}	41
7.0 × 10 ^{−3}	2.6 × 10 ^{−3}	41

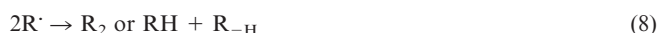
The results clearly indicate that total debromination is obtained at low concentrations of (CH₂Br)₂C(CH₂OH)₂ and therefore only lower limits of G(Br[−]) can be derived. The yield of Br[−] is considerably larger than the primary yield of radicals, G = 6.0,^[10] therefore it has to be concluded that the debromination occurs via a chain reaction.

When blank experiments were performed (in the absence of (Ni^{II}L)²⁺ surprisingly G(Br[−]) = 112 was obtained.^[18]

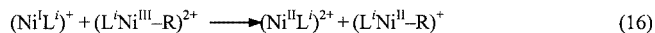
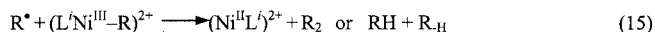
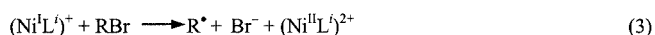
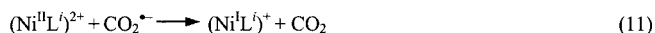
These results are in agreement with the following mechanism:^[18]



and the termination reactions:



In the presence of (Ni^{II}L)²⁺ the following reactions have to be added:



Thus the nickel complex “retards” the radiolytic debromination reactions, as reactions (13) and (15) are also termination steps.

Electrochemical Studies

The complexes $(\text{Ni}^{\text{II}}\text{L}^i)^{2+}$ were electrochemically (CV experiments) reduced on a glassy carbon electrode in He-saturated aqueous solutions, at pH 10, using NaClO_4 as the supporting electrolyte. Cyclic voltammograms show pseudo-reversible waves which correspond to the $\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}}$ redox couples. Under the same conditions $(\text{CH}_2\text{Br})_2\text{C}(\text{CH}_2\text{OH})_2$ is not reduced in the voltage range required for the reduction of the $(\text{Ni}^{\text{II}}\text{L}^i)^{2+}$ complexes. When $(\text{CH}_2\text{Br})_2\text{C}(\text{CH}_2\text{OH})_2$ is added, at different concentrations — $(2-7) \times 10^{-3} \text{ M}$ — to a solution containing $5 \times 10^{-4} \text{ M}$ $(\text{Ni}^{\text{II}}\text{L}^i)^{2+}$ complex, the voltammetric behavior of $(\text{Ni}^{\text{II}}\text{L}^i)^{2+}$ changes. On addition of low concentrations of $(\text{CH}_2\text{Br})_2\text{C}(\text{CH}_2\text{OH})_2$, the reduction current of the cathodic peak ($\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}}$) is enhanced in comparison with the reference voltammogram of $(\text{Ni}^{\text{II}}\text{L}^i)^{2+}$ alone, whereas that of the anodic peak decreases. On further addition of substrate, the cathodic peak current increases further and no anodic current is observed on the reverse scan, showing that $(\text{CH}_2\text{Br})_2\text{C}(\text{CH}_2\text{OH})_2$ is efficiently reduced electrocatalytically (Figure 5).

The increase in the cathodic peak current is linearly proportional to the concentration of the substrate, suggesting that the electrochemical process is diffusion controlled. This conclusion is in agreement with the rate constants of reaction (3) in Table 1. Thus, the nickel complexes are good electrocatalysts for the reduction of $(\text{CH}_2\text{Br})_2\text{C}(\text{CH}_2\text{OH})_2$.

As the concentration of $(\text{Ni}^{\text{II}}\text{L}^i)^{2+}$ is expected to be low near the electrode, the electrochemical process is probably best described by reaction:



followed by reactions (3), (12) or (14) + (16) and (13).

Preparative electrolysis was carried out at several potentials in the presence of $(\text{Ni}^{\text{II}}\text{L}^3)^{2+}$ as the electrocatalyst. The

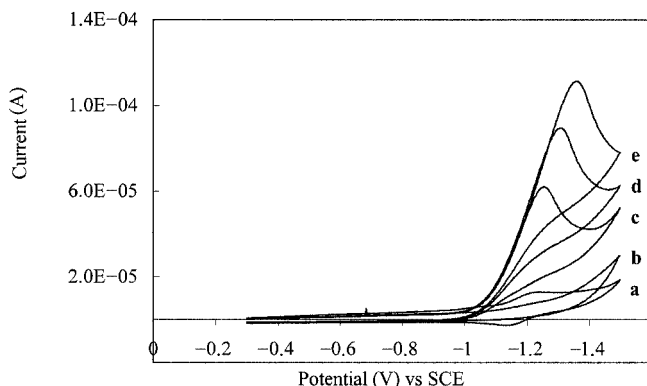


Figure 5. Cyclic voltammograms at pH 10.0 ± 0.3 , supporting electrolyte 0.01 M NaClO_4 , scan rate 50 mV/s : (a) $5 \times 10^{-4} \text{ M}$ $(\text{Ni}^{\text{II}}\text{L}^3)^{2+}$; (b) $7 \times 10^{-3} \text{ M}$ $(\text{CH}_2\text{Br})_2\text{C}(\text{CH}_2\text{OH})_2$; (c) (a) + $3 \times 10^{-3} \text{ M}$ $(\text{CH}_2\text{Br})_2\text{C}(\text{CH}_2\text{OH})_2$; (d) (a) + $5 \times 10^{-3} \text{ M}$ $(\text{CH}_2\text{Br})_2\text{C}(\text{CH}_2\text{OH})_2$; (e) (a) + $7 \times 10^{-3} \text{ M}$ $(\text{CH}_2\text{Br})_2\text{C}(\text{CH}_2\text{OH})_2$

maximum of the reduction peak for this complex, using a graphite electrode, is observed at -1.15 V . The concentration ratio $\text{RBr}/(\text{Ni}^{\text{II}}\text{L}^3)^{2+}$ was 10. The results of the yield of Br^- as a function of the applied potentials are summarized in Table 3. As expected, the yield of Br^- increases upon shifting the potential cathodically.

Table 3. Bromide yield as function of potential; solution composition: 0.1 M NaClO_4 , $5 \times 10^{-4} \text{ M}$ $(\text{Ni}^{\text{II}}\text{L}^3)^{2+}$ and $5 \times 10^{-3} \text{ M}$ $(\text{CH}_2\text{Br})_2\text{C}(\text{CH}_2\text{OH})_2$, pH 10.0 ± 0.3 , He sat.; experimental error: $\pm 20\%$

Potential (V)	-1.00	-1.05	-1.10	-1.15	-1.22	-1.30
$[\text{Br}^-] \text{ (M)}$	0.00026	0.00055	0.0013	0.0022	0.0028	0.0034

Concluding Remarks

The results presented here elucidate the mechanism of the electrocatalytic debromination processes. The rate of the debromination step, reaction (3), depends mainly on the redox potential of the $\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}}$ couple. It is proposed that these nickel complexes may be bound to modified electrodes, and might be useful as electrocatalysts for the dehalogenation of aliphatic halo-organic compounds.

Surprisingly enough it is shown that formate reduces $(\text{CH}_2\text{Br})_2\text{C}(\text{CH}_2\text{OH})_2$ in a radical-induced catalytic process, i.e. formate acts via a hydrogen-atom-transfer mechanism.

Experimental Section

Materials: All solutions were prepared from analytical-grade chemicals and distilled water that was passed through a Millipore setup, the final resistance being above $10 \text{ M}\Omega$.

The complexes $\text{Ni}^{\text{II}}\text{L}^i(\text{ClO}_4)_2$ ($i = 1-4$) were prepared according to literature procedures,^[8,19] and were characterized by NMR, UV/Vis and IR spectroscopy.

Warning: Transition metal perchlorates are potentially explosive and have to be handled with care.

Pulse Radiolysis: The solutions were handled by the syringe technique.^[20] The experiments were carried out using the Varian 7715 linear accelerator facility of the Hebrew University of Jerusalem. The pulse duration was $0.5-1.5 \mu\text{s}$ with a 200 mA current of 5 MeV electrons. The dose per pulse was in the range of $10-30 \text{ Gy/pulse}$. The experimental setup and the techniques used for evaluating the results have been described in detail elsewhere.^[21,22]

Electrochemical Measurements: The electrochemical experiments were carried out using an EG&G Potentiostat/Galvanostat Model 263. A three-electrode cell was used. The working electrode was a glassy carbon electrode of 3 mm diameter, the auxiliary electrode was a Pt wire and an SCE was used as the reference electrode.

The preparative electrolyses were performed at controlled potential conditions in a three-electrode cell. A graphite electrode was used as the cathode. The counter electrode was a Pt wire and the satu-

rated calomel electrode (SCE) served as a reference electrode. 0.1 M NaClO₄ was used as a support electrolyte. The experiments were performed with constant stirring.

Product Analysis: Quantitative analysis of bromide was performed by ion chromatography on a Hamilton-PRP-X100 column (250 × 4.1 mm²) using a Jasco PU-980 Intelligent HPLC Pump and was optimized utilizing H₅C₆CO₂Na (4 mM) as the eluent. The flow rate was 1.5 mL/min and a suppressed conductivity detector was used.

Irradiation: γ-Irradiations were carried out in a ⁶⁰Co γ source, Noratom, with a dose rate of about 4.0 Gy/min, which was determined by means of Fricke dosimetry, using a G value of G = 15.6.^[23,24]

Acknowledgments

This study was supported in part by a grant from the Budgeting and Planning Committee of The Council of Higher Education and the Israel Atomic Energy Commission. D. M. wishes to express his thanks to Mrs. Irene Evens for her ongoing interest and support.

- [1] National Academy of Sciences. *Alternatives for ground water cleanup*; National Academy Press: Washington, DC **1994**.
- [2] H. Kerndorff, in *Chemie und Biologie der Altlasten*; Fachgruppe Wasserchemie der GDCh, VCH: Weinheim **1997**, 1–41.
- [3] R. Mertens, C. Sonntag, *J. Chem. Soc., Perkin Trans. 2* **1994**, 2181–2185.
- [4] A. Bakac, J. H. Espenson, *J. Am. Chem. Soc.* **1986**, 108, 713–719.
- [5] M. S. Ram, A. Bakac, J. H. Espenson, *Inorg. Chem.* **1986**, 25, 3267–3272.
- [6] J. Y. Becker, J. B. Kerr, D. Pletcher, R. Rosas, *J. Electroanal. Chem.* **1981**, 117, 87–99.

- [7] C. Gosden, J. B. Kerr, D. Pletcher, R. Rosas, *J. Electroanal. Chem.* **1981**, 117, 101–107.
- [8] N. Jubran, G. Ginzburg, H. Cohen, Y. Korehs, D. Meyerstein, *Inorg. Chem.* **1985**, 24, 251–258.
- [9] D. Meyerstein, *Coordin. Chem. Rev.* **1999**, 185–186, 141–147.
- [10] M. S. Matheson, L. M. Dorfman, *Pulse Radiolysis*, MIT Press, Cambridge, MA, **1969**.
- [11] G. V. Buxton, C. L. Greenstock, W. P. Helman, A. B. Ross, *J. Phys. Chem. Ref. Data* **1988**, 17, 513–886.
- [12] P. Wardman, *J. Phys. Chem. Ref. Data* **1989**, 18, 1637–1755.
- [13] H. A. Schwarz, R. W. Dodson, *J. Phys. Chem.* **1989**, 93, 409–414.
- [14] C. Creutz, H. A. Schwarz, J. F. Wishart, E. Fujita, N. Sutin, *J. Am. Chem. Soc.* **1991**, 113, 3361–3371.
- [15] I. Zilbermann, M. Winnik, D. Sagiv, A. Rotman, H. Cohen, D. Meyerstein, *Inorg. Chim. Acta* **1995**, 240, 503–514.
- [16] A. Sauer, H. Cohen, D. Meyerstein, *Inorg. Chem.* **1988**, 27, 4578–4581.
- [17] R. V. Eldik, H. Cohen, A. Meshulam, D. Meyerstein, *Inorg. Chem.* **1990**, 29, 4156–4158.
- [18] E. Shandalov, I. Zilbermann, E. Maimon, Y. Nahmani, H. Cohen, E. Adar, D. Meyerstein, to be published.
- [19] M. P. Suh, H. Y. Kim, M. J. Kim, K. Y. Oh, *Inorg. Chem.* **1992**, 31, 3620–3625.
- [20] E. J. Hart, S. Gordon, J. K. Thomas, *J. Phys. Chem.* **1964**, 68, 1271–1274.
- [21] S. Goldstein, G. Czapski, H. Cohen, D. Meyerstein, J. K. Cho, S. S. Shaik, *Inorg. Chem.* **1992**, 31, 798–803.
- [22] N. Shaham, A. Masarwa, Y. Matana, H. Cohen, D. Meyerstein, *Eur. J. Inorg. Chem.* **2002**, 87–92.
- [23] E. J. Hart, *Radiat. Res.* **1955**, 2, 33–46.
- [24] H. Fricke and E. J. Hart, in *Radiation Dosimetry* (Eds.: F. H. Attix, W. C. Roesch and E. Tochilin), Academic Press, New York, **1966**, p. 167.

Received February 27, 2003
Early View Article
Published Online October 2, 2003