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Reduction of Ethylene by $Ni^I(cyclam)^+$ in Aqueous Solutions[†]

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Ni^I(1,4,8,11-tetraazacyclotetradecane)$^+$ reduces ethylene quantitatively to ethane plus butane (and hexane traces) in neutral aqueous solutions. A radical mechanism is proposed.

Introduction

It was recently shown[1] that the central Ni(I) cation in the complex Ni^I(1,8-di-2-propenyl-1,4,8,11-tetraazacyclotetradecane)$^+$ reduces the propenyl substituents in neutral aqueous solutions. Due to the importance of the hydrogenation of alkenes and due to the environmental advantage of carrying out such reactions in aqueous solutions, it seemed of interest to check whether Ni^I(1,4,8,11-tetraazacyclotetradecane)$^+$, NiL^+, reduces alkenes dissolved in aqueous solutions. If such reductions indeed occur, then by changing the redox potential of the complex by either changing the structure of the ligand[2] or using another central cation, one plausibly will be able to reduce selectively a given double bond in a substrate without reducing other double bonds. Furthermore, then one will plausibly be able to hydrogenate alkenes selectively electrochemically[1] in aqueous solutions.

Experimental Section

All of the chemicals used were of analytical grade, purchased from Aldrich or Fluka, and were used as is. Solutions were prepared in deionized water, which was further purified by passing through a MilliQ system by Millipore and had a resistance of ≥ 10 MΩcm^{-1}. The C_2H_4 gas was purchased from Maxima, Israel, and was passed through two washing bottles, containing 0.1 M V^{2+} in dilute H_2SO_4 over a Zn amalgam and pure water in order to remove traces of dioxygen. The ligand L = 1,4,8,11-tetraazacyclotetradecane and the complex $NiL(ClO_4)_2$ were synthesised according to literature procedures[3] and characterized by NMR and UV−vis spectroscopy.[3]

Samples, in small glass vials, stoppered with a rubber septum, were irradiated in a ^{60}Co γ source by Noratom with an average dose rate of 3.0 Gy/min during this study. The product gases were analyzed by GC using a Varian Model Star 3600CX with a FID. The gases were separated on a Supelco 10 ft long 0.25 inch diameter column with a Poropaq QS 5080 Mesh filling. The carrier gas was He with a flow rate of 40 mL/min. The detector temperature was 290 °C, and the column temperature was 60 °C for 3.5 min and then was raised by 40 °C/min up to 160 °C and was kept at this temperature throughout the analysis. The ignition temperature was 70 °C.

Pulse radiolysis experiments were performed using the same setup and procedures described in detail earlier.[4,5]

TABLE 1: Gaseous Products in Irradiated Samples[a]

$[NiL^{2+}]$, M	total dose, Gy	C_2H_6 yield, *G*	C_4H_{10} yield, *G*
−	100	0.62	0.06
−	400	0.45	0.06
5×10^{-4}	100	1.5	0.14
5×10^{-4}	400[b]	2.0	0.17

[a] C_2H_4 solutions containing 0.3 M $NaHCO_2$ and 0.01 M phosphate at pH 6.1. The accuracy is ±10%. [b] In these samples, traces of C_6H_{14} were detected.

Ionizing Radiation As a Source of Reducing Radicals. When neutral dilute aqueous solutions are irradiated by ionizing radiation, the following primary products are formed:[6]

$$H_2O \xrightarrow{\gamma, e^-} {}^\bullet OH\ (2.65),\ e^-_{aq}\ (2.65),\ {}^\bullet H\ (0.60),\ H_2\ (0.45),\ H_2O_2\ (0.75),\ H_3O^+\ (2.65) \quad (1)$$

The yield of the products is reported as *G* values, which are the number of product molecules (species) formed per 100 eV of radiation absorbed in the sample. The values in parentheses in eq 1 are the *G* values for the different primary products in dilute aqueous solutions.[6] In concentrated solutions the "radical" (${}^\bullet OH$, e^-_{aq}) yields are somewhat higher, and the "molecular" (H_2, H_2O_2, and ${}^\bullet H$) are somewhat lower.[6]

When formate is added to the irradiated solutions, it reacts with the ${}^\bullet OH$ radicals and the H atoms via[7]

$$HCO_2^- + {}^\bullet OH/{}^\bullet H \rightarrow CO_2{}^{\bullet -} + H_2O/H_2$$
$$k_{\bullet OH} = 3.2 \times 10^9\ M^{-1}\ s^{-1}$$
$$k_{\bullet H} = 2.1 \times 10^8\ M^{-1}\ s^{-1} \quad (2)$$

transforming the strong oxidizing agent, ${}^\bullet OH$ radicals, in a reducing agent, $CO_2{}^{\bullet -}$ anion radicals. Thus, in these solutions, there remains only two strong reducing radicals e^-_{aq}, $E° = -2.87$ V versus SHE[8] and $CO_2{}^{\bullet -}$, $E° = -1.9$ V versus SHE.[8]

We could not use N_2O saturated solutions, in which all of the primary radicals are transformed into $CO_2{}^{\bullet -}$ anion radicals, as NiL^+ reacts in a fast reaction with N_2O.[9]

Results and Discussion

C_2H_4 saturated solutions containing 0.3 M $HCO_2^-Na^+$ and 0.01 M phosphate buffer at pH 6.1 in the presence and absence of $NiL(ClO_4)_2$[10] were irradiated in the γ-source, and the product gases were determined by GC; the results are summed up in Table 1.

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In these solutions, the $CO_2{\cdot}^-$ and e^-_{aq} radical anions reduce the NiL^{2+} via[9]

$$NiL^{2+} + e^-_{aq} \rightarrow NiL^+_{aq} \qquad k = 3.8 \times 10^{10}\ M^{-1}\ s^{-1} \quad (3)$$

$$NiL^{2+} + CO_2{\cdot}^- \rightarrow NiL^+_{aq} + CO_2 \qquad k = 5.2 \times 10^{9}\ M^{-1}\ s^{-1} \quad (4)$$

Thus, the expected yield of NiL^+_{aq} is $G(NiL^+_{aq}) = 6.0$; see the Experimental Section. However, as NiL^+_{aq} reacts via a fast reaction with H_2O_2, remembering that $G(H_2O_2) = 0.75$ and assuming that two NiL^+ species are oxidized by one H_2O_2 molecule,[1,11] the yield of NiL^+ available for the reduction of C_2H_4 is $G(NiL^+_{aq}) = 4.5$. As the reduction of C_2H_4 to form C_2H_6 or C_4H_{10} requires two electrons for each product molecule, one expects $G(C_2H_6 + C_4H_{10}) = 2.25$. The experimental result in the samples irradiated by 400 Gy is $G(C_2H_6 + C_4H_{10}) = 2.17 \pm 10\%$. Thus, clearly all of the NiL^+_{aq} produced by the irradiation reduces the C_2H_4. (The somewhat smaller yields obtained in the samples irradiated by the lower dose are probably due to some oxidizing impurity present in the samples; e.g. 2.5×10^{-6} M O_2 would cause such an effect.)

In an effort to gain further mechanistic information on the mechanisms of this process, pulse-radiolytic experiments were performed. However, under the experimental conditions, saturation of the solutions by C_2H_4 instead of Ar accelerated the apparent second-order rate constant of the disappearance of NiL^+ only from $2k_{obs} = 9.8 \times 10^4\ M^{-1}\ s^{-1}$ to $2k_{obs} = 2.7 \times 10^5\ M^{-1}\ s^{-1}$. This small effect rules out a detailed mechanistic study. Furthermore, the results suggest that the rate constant of the reduction of C_2H_4 by NiL^+ is relatively slow. Therefore, high reduction yields, quantitative ones, are achieved only by the application of the low-dose-rate γ-source.

Finally, it is tempting to speculate on the mechanism of reduction. The first step probably involves the formation of a d → π^* complex between the low-valent NiL^+ complex and the ethylene

$$NiL(H_2O)_2 + C_2H_4 \overset{K_5}{\rightleftharpoons} ((H_2O)LNi{-}||)^+ \quad (5)$$

The value of the stability constant, K_5, is probably not high as no spectral changes were observed during the reaction time, though the rate constants of the axial ligand exchange of the Jahn−Teller-distorted $LNi(H_2O)_2^+$ complex are probably very high.

The following reaction is probably

$$((H_2O)LNi{-}||)^+ \xrightarrow{\cdot H^+} \begin{array}{l} \rightarrow NiL^{2+} + {\cdot}CH_2CH_3 \\ \rightarrow (H_2O)LNi^{III}{-}CH_2CH_3 \end{array} \quad (6)$$

which is followed by

$$NiL^{2+} + {\cdot}CH_2CH_3 \overset{K_7}{\rightleftharpoons} (H_2O)LNi^{III}{-}CH_2CH_3 \quad (7)$$

The value of K_7 is probably relatively high as[12,13]

$$NiL^{2+} + {\cdot}CH_3 \overset{K_{7'}}{\rightleftharpoons} (H_2O)LNi^{III}{-}CH_3^{2+} \qquad K_{7'} = 1.1 \times 10^7\ M^{-1} \quad (7')$$

The ethane is then most probably formed via

$$NiL(H_2O)_2 + (H_2O)LNi^{III}{-}CH_2CH_3^{2+} \rightarrow NiL^{2+} + LNi^{II}{-}CH_2CH_3{}^+_{aq} \quad (8)$$

$$LNi^{II}{-}CH_2CH_3{}^+_{aq} \xrightarrow{H^+} NiL^{2+} + C_2H_6 \quad (9)$$

These reactions are proposed as heterolysis of the $Ni^{II}{-}C$ bonds is well documented,[14] whereas $Ni^{III}{-}C$ bonds are known to decompose via homolysis.[14]

The butane is probably formed either via

$$2{\cdot}C_2H_5 \rightarrow C_4H_{10} \quad (10)$$

in analogy to the formation of C_2H_6 in the decomposition of $(H_2O)LNi^{III}{-}CH_3^{2+}$ [10,11] or via

$$(H_2O)LNi^{III}{-}CH_2CH_3{}^{2+}_{aq} + {\cdot}C_2H_5 \rightarrow NiL^{2+} + C_4H_{10} \quad (11)$$

a reaction which was not observed in the $(H_2O)LNi^{III}{-}CH_3^{2+}$ system.

As $NiL(H_2O)_2^+$ is formed continuously under the experimental conditions, reaction 8 competes well with reactions 10 and 11, and therefore, the yield of C_2H_6 is considerably larger than that of C_4H_{10}.

Alternatively, C_4H_{10} might be formed via

$$(H_2O)LNi^{II}{-}CH_2CH_3^{2+} + C_2H_4 \rightarrow \textit{cis}\text{-}LNi^{II}(C_2H_4)CH_2CH_3^{+} \rightarrow (H_2O)LNi^{II}{-}C_4H_9 \rightarrow NiL^{2+} + C_4H_{10} \quad (12)$$

This reaction requires an isomerization of the *trans*-Ni(II)complex to form the cis isomer.

Also, the reaction

$$((H_2O)LNi{-}||)^+ + {\cdot}C_2H_5 \rightarrow (H_2O)LNi^{II}{-}C_4H_9^{+} \quad (13)$$

cannot be ruled out.

The formation of traces of C_6H_{14} clearly proceeds via analogous reactions. The formation of C_4H_{10} and C_6H_{14} proves that the radicals ${\cdot}C_2H_5$ and ${\cdot}C_4H_9$ are intermediates in the reduction mechanism.

Conclusions

The results clearly point out that $NiL(H_2O)_2^+$ reduces ethylene in aqueous solutions. This result suggests that NiL^{2+} can be used as an electrocatalyst for the hydrogenation of alkenes in aqueous solutions.

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References and Notes

(1) Raznoshik, H.; Zilberman, I.; Maimon, E.; Ellern, A.; Cohen, H.; Meyerstein, D. *Inorg. Chem.* **2003**, *42*, 7156–7161.

(2) Busch, D. H.; Pillsbury, D. G.; Lovecchio, F. V.; Tait, A. M.; Hung, Y.; Jackels, S.; Rakowski, M. C.; Schammel, W. P.; Martin, L. Y. *ACS Symp. Ser. Electrochem. Stud. Biol. Syst., Symp.* **1976**, *38*, 32–50.

(3) Barefield, E. K.; Wagner, F.; Herlinger, A. W.; Dahl, A. R. *Inorg. Synth.* **1976**, *16*, 220–225.

(4) Goldstein, S.; Czapski, G.; Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1992**, *31*, 2439–2444.

(5) Freiberg, M.; Meyerstein, D. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1825–1837.

(6) Matheson, M. S.; Dorfman, L. *Pulse Radiolysis*; M.I.T. Press: Cambridge, MA, 1969.

(7) Buxton, G. V.; Greenstock, C. V.; Helman, W. P.; Ross, A. R. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513–886.

(8) Wardman, P. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1637–1755.

(9) Jubran, N.; Ginzburg, G.; Cohen, H.; Koresh, Y.; Meyerstein, D. *Inorg. Chem.* **1985**, *24*, 251–258.

(10) No spectral changes were observed when ethylene was bubbled into the nickel-containing solution, that is, the d−d band was not affected. This result points out that ethylene does not form a complex with the low-spin $Ni^{II}(cyclam)^{2+}$, as expected for this complex which has a very low tendency to bind axial ligands. Even if a small fraction of such a complex would be formed, the radical anions e^-_{aq} and $CO_2{\cdot}^-$would not react with this complex due to the high rate constant of reactions 3 and 4.

(11) One of the reviewers suggested that the reaction of $Ni(I)L^+$ with H_2O_2 might start a chain reaction and clearly should not reduce the decrease in the ethylene consumption. This suggestion contradicts the experimental observations in ref 1 and in this note. This suggestion is based on the assumption that the reaction of Ni^IL^+ with H_2O_2 will produce radicals. However, two-electron oxidations of Ni^IL^+, for example, by N_2O, were reported. Alternatively, the complex $Ni^IL{\cdot}H_2O_2$ might react with another Ni^IL complex prior to decomposition.

(12) Kurzion-Zilbermann, T.; Masarwa, A.; Maimon, E.; Cohen, H.; Meyerstein, D. *Dalton Trans.* **2007**, 3959–3965.

(13) Sauer, A.; Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1988**, *27*, 4578–4581.

(14) Masarwa, A.; Meyerstein, D. *Advances in Inorganic Chemistry: Including Bioinorganic Studies*; 2004; Vol. 55, pp 271−313.

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