rate in the Co^I neutral complexes but not in the Co^0 anion radicals. This argues that the isomerization mechanism is different in the two different metal oxidation states.

2. The rapid isomerization of the Co^0 complexes may arise from lifting of symmetry restrictions to the simplest molecular isomerization mechanism in the 19-electron monoanions.

3. When dibenzocyclooctatetraene is used as the ligand, the Co^0 monoanion has a different ground state than $[CpCo(cot)]^-$, and CpCo(dbcot) behaves more like a cod complex with electron-withdrawing substituents. The activation barrier to isomerization in $[CpCo(dbcot)]^-$ is raised at least 9.4 kcal/mol over that of $[CpCo(cot)]^-$, a value consistent with the necessity to break up aromatic resonance in a 1,3-isomer of CpCo(dbcot).

Acknowledgment. This work was generously supported by the National Science Foundation (CHE 83-03974). We are grateful to J. L. Spencer for an initial sample of **2**, to J. Edwin for help on the synthesis of dbcot, and to C. H. Bushweller for aid in simulations of dynamic NMR spectra. A.S. wishes to acknowledge the support of the Swiss National Science Foundation (2.165-0.83).

Electrocatalytic Reduction of CO_2 by Ni Cyclam^{2+} in Water: Study of the Factors Affecting the Efficiency and the Selectivity of the Process

Marc Beley, Jean-Paul Collin, Romain Ruppert, and Jean-Pierre Sauvage*

Contribution from the Laboratoire de Chimie Organo-Minérale, UA 422 au CNRS, Institut de Chimie, 67000 Strasbourg, France. *Received February 10, 1986*

Abstract: The electrocatalytic properties of Ni cyclam^{2+} in CO_2 reduction have been studied. The influence of various experimental factors on the course of the reaction has been investigated. Under given conditions, Ni cyclam^{2+} is remarkably efficient and selective for electroreduction of CO_2 into CO, even in water. The stability of the system has been tested in long range electrolysis, showing that even after thousands of catalytic cycles no deactivation occurs. The mechanistic investigation presently described points to the importance of molecular species adsorbed on the cathode surface. The contribution of reduced species in the bulk is marginal. In addition, during the electrocatalytic process, a nickel(I) carbonyl complex is present: $[Ni(cyclam)(CO)]^+$. The latter complex may be involved in the catalytic reaction leading to CO evolution. Surprisingly, the behavior of Ni cyclam^{2+} as electrocatalyst is unique. Among the numerous complexes investigated, only Ni cyclam^{2+} shows such a large selectivity for the electroreduction of CO_2 over the electroreduction of water. The size of the cyclam ligand and the presence of secondary amine groups (NH) might account for the very special properties of the electrocatalyst.

The transformation of CO_2 into organic substances is a promising long term objective. It could allow the preparation of fuels or chemicals from a cheap and abundent carbon source. Among various possible approaches, the electrochemical reduction of CO_2 appears to be an attractive method. Indeed, studies on the electrochemical reduction of CO_2 on a metallic cathode were begun as early as the nineteenth century[1] or very early this century.[2] The main product was found to be formic acid. Early studies on CO_2 electroreduction in aqueous media are discussed in an excellent review and references cited therein.[3]

The electrochemical reduction of CO_2 on mercury or on lead in low protic medium was also performed.[4] More recent investigations have been carried out with various cathodic materials.[5] In particular, indium was claimed to be an interesting material, allowing CO_2 electroreduction with a very low overvoltage.[6] Electroanalytical studies on tin and indium have recently been carried out.[7] Unfortunately, indium does not seem to display the catalytic properties previously postulated, as shown by further investigations.[8,9] Use of rhodium[10] and ruthenium[11] cathodes gave low overpotentials, but with such materials, whose catalytic properties for H_2O reduction to H_2 are excellent, the selectivity of CO_2 electroreduction in aqueous medium is expected to be low. In addition, the catalytic nature of the process using ruthenium cathodes[11] remains to be proven, although highly reduced products (CH_4 and CH_3OH) are found, making the ruthenium cathode a promising system. Semiconductors have also been used as cathodic materials, either in the dark[12-14] or under light irradiation. In the latter case, semiconductor suspensions have been used,[15-19] or the reaction has been performed in a photoelectrochemical cell

---

[1] Royer, M. E. *Compt. Rend. Hebd. Séances Acad. Sci.* **1870**, *70*, 731.

[2] Cohen, A.; Jahn, S. *Chem. Ber.* **1904**, *37*, 283. Ehrenfeld, R. *Chem. Ber.* **1905**, *38*, 4138.

[3] Russel, P. G.; Kovac, N.; Srinivasan, S.; Steinberg, M. *J. Electrochem. Soc.* **1977**, *124*, 1329.

[4] Gressin, J. C.; Michelet, D.; Nadjo, L.; Savéant, J. M. *Nouv. J. Chim.* **1979**, *3*, 545.

[5] Eggins, B. R.; McNeill, J. *J. Electroanal. Chem.* **1983**, *148*, 17.

[6] Ito, K.; Murata, T.; Ikedo, S. *Nagoya Kogyo Daigaku Gakuho* **1975**, *27*, 209.

[7] Kapusta, S.; Hackerman, N. *J. Electrochem. Soc.* **1983**, *130*, 607.

[8] Taniguchi, I.; Aurian-Blajeni, B.; Bockris, J. O.'M. *J. Electroanal. Chem.* **1983**, *157*, 179.

[9] Beley, M.; Chabrand, C.; Collin, J. P.; Rieux, C.; Ruppert, R.; Sauvage, J. P., unpublished results.

[10] Sobkowski, J.; Wieckowski, A.; Zelenay, P.; Czerwinski, A. *J. Electroanal.* **1979**, *100*, 781.

[11] Frese, K. W.; Leach, S. *J. Electrochem. Soc.* **1985**, *132*, 259.

[12] Monnier, A.; Augustynski, J.; Stalder, C. *J. Electroanal. Chem.* **1980**, *112*, 383.

[13] Koudelka, M.; Monnier, A.; Augustynski, J. *J. Electrochem. Soc.* **1984**, *131*, 745.

[14] Frese, K. W.; Canfield, D. *J. Electrochem. Soc.* **1984**, *131*, 2518.

[15] Halmann, M. *Nature (London)* **1978**, *275*, 115.

[16] Inoue, T.; Fuhishima, A.; Konishi, S.; Honda, K. *Nature (London)* **1979**, *277*, 637.

[17] Ulman, M.; Aurian-Blajeni, B.; Halmann, M. *Isr. J. Chem.* **1982**, *22*, 177.

[18] Taniguchi, Y.; Yoneyama, H.; Tamura, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2034.

[19] Chandrasekaran, K.; Thomas, J. K. *Chem. Phys. Lett.* **1983**, *99*, 7.

0002-7863/86/1508-7461$01.50/0

Table I. Electrochemical Reduction of CO_2 to CO in Water: Study of the Efficiency and Selectivity of the Process[a]

expt	electrctlyst	*E* (V vs. NHE)	tot. vol of CO prodcd (mL)	turnover freq on Ni cyclam^{2+} (h^{-1})	current effcncy (%)	H_2:CO in gas prodcd
1	$NiCl_2 \cdot 6H_2O$	−1.05	0.05			
2	Ni cyclam Cl_2	−0.90	0.4	0.3	36	2×10^{-2}
3	Ni cyclam Cl_2	−0.95	3.6	2.9	82	3×10^{-3}
4	Ni cyclam Cl_2	−1.00	24.0	18	99	5×10^{-4}
5	Ni cyclam Cl_2	−1.05	36.0	32	96	3×10^{-4}

[a] For experimental conditions, see Experimental Section; [Ni cyclam^{2+}] = 1.7×10^{-4} M in 0.1 M KNO_3 (pH 4.1). Electrolysis time: 4 h. For experiment 4 $\bar{i}$ = 0.7 mA/cm^2.

with a semiconductor cathode.[20-25]

Generally, the electrochemical reduction of CO_2 on metallic cathodes requires very negative potentials. Typically, potentials below −2V vs. NHE must be applied in order to lead to noticeable current densities. In order to reduce energy consumption, catalytic species must be used in conjunction with the cathode. The use of molecular electrocatalysts is promising in many respects, because of the selectivity and efficiency associated with homogeneous catalysis. In addition, subtle variations in the structure of the molecular relay may be readily introduced by appropriate synthetic procedures. The first attempts have been reported by Japanese workers.[26] Cobalt or nickel phthalocyanines were shown by electroanalytical methods to exhibit electrocatalytic properties for the reduction of CO_2. For similar studies performed later on sulfonated cobalt or nickel phthalocyanines[27] or porphyrins,[28] no chemical analyses of the reduction products were reported. The first convincing results were published in 1980 by Fischer and Eisenberg.[29] They used various tetraazamacrocyclic complexes of Co or Ni as electrocatalysts on a mercury pool as cathodes in a mixed solvent (CH_3CN–H_2O). CO was shown to be the major product of the reduction. Faradaic yields for CO generation were found to be in the range of 40–50%. Recently, further studies with metallophthalocyanines (Co or Ni) deposited on carbon electrodes have shown that CO_2 is mainly reduced to CO or formate ion.[30,31] Interestingly, several macrocyclic complexes could be used in photoelectrochemical systems with semiconductors (p-Si,[32] p-Gap,[33] or p-GaAs[33]), CO_2 being reduced to CO at relatively low negative potentials.

In recent years, various acyclic complexes have been proposed as electrocatalysts including an iron–sulfur cluster,[34] complexes of rhenium,[35] rhodium,[36,37] or ruthenium.[37] There are several reports which do not use transition-metal complexes as catalysts but which are built on a similar approach: when a derivative of MV^{2+} (MV^{2+} = methylviologen or *N,N′*-dimethyl-4,4′-bipyridium ion) is used as electron relay in association with a heterogeneous catalyst[38] (palladium) or a formate dehydrogenase enzyme,[39] formate is obtained from bicarbonate or CO_2. It is worth noting that photochemical molecular systems recently developed for reducing CO_2[40-42] are somewhat related to the electrocatalytic approach.

In order to obtain a useful electrocatalyst, several prerequisites must be fulfilled, and, in particular, the selectivity of the process is highly important. The vast majority of electrochemical systems available for reducing CO_2 require the presence of water. As a consequence, its reduction to molecular hydrogen will always be a competing reaction to be avoided. We have recently reported the exceptional efficiency and selectivity of nickel(II) cyclam (cyclam = 1,4,8,11-tetraazatetradecane) as an electrocatalyst for the reduction of CO_2, even in water.[43] We now present a more detailed study of the reaction, and its mechanistic aspects are substantiated by experimental results. Investigations of the efficiency and stability of the electrocatalysts show that Ni cyclam^{2+} is superior to analogous complexes. Cyclam is an attractive ligand because of its accessibility and the exceptional kinetic and thermodynamic stability of its complexes,[44] in particular those with Ni^{2+}.

Experimental Section

Materials. Aqueous solutions were prepared from analytical grade salts and doubly distilled water. Ni cyclam Cl_2 and all the other tetraazacomplexes of nickel(II) and cobalt(II) were prepared to previously reported procedures.[45] Dimethylformamide (DMF) was dried overnight over P_2O_5 and distilled under vacuum. The following gases (Air Liquide) were used without further purification: nitrogen (99.998%), argon (99.995%), carbon monoxide (99.995%), carbon dioxide (99.995%), and methane (99.995%).

Analytic Methods. Gas samples (500 μL), taken at various intervals with a gas-tight syringe through a septum and a valve, were analyzed on a Varian Autoprep 700 gas chromatograph with a thermal conductivity detector by using a 10 m × $^1/_4$ in. column packed with molecular sieve 13X (LINDE) at 25 °C using methane as carrier gas. The detection limits for CO and H_2 are respectively 0.2% and 0.01%. Formaldehyde and formic acid were determined by a colorimetric method.[46] Even for long term electrolysis, their formation was almost completely negligable (< 0.3 μmol).

Spectroscopic Measurements. Electronic spectra were performed in a quartz cell mounted on a schlenck tube. A Cary 118 or 219 spectrophotometer was used. Solution infrared spectra were obtained by using sodium chloride plates on a Perkin Elmer 597 spectrometer.

EPR spectra were plotted on a Bruker ER 420 spectrometer at 77 K.

Electrochemical Measurements. Controlled-potential coulometric experiments were performed at 25 °C, in a gas-tight electrolysis cell under one atmosphere of CO_2 (or N_2) with a Tacussel PRT 40.1-X potentiostat and a coulometric integrator (Tacussel IG 5-LN). The gas-tight cell was a 100-mL, three-necked, round-bottomed flask equipped with two sidearms. The working electrode in all the experiments was mercury (18 cm^2; purity: 99.99999%). The counter electrode (Pt) and the reference electrode (SCE) were separated from the working electrode compartment by glass frits. The cell volume was 160 mL, 85 mL of which was occu-

---

(20) Taniguchi, Y.; Yoneyama, H.; Tamura, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2934.

(21) Aurian-Blajeni, I. B.; Halmann, M.; Manassen. J. *Sol. Energy Mater.* **1983**, *8*, 425.

(22) Aurian-Blajeni, B.; Taniguchi, I.; Bockris, J. O'M. *J. Electroanal. Chem.* **1983**, *149*, 291.

(23) Taniguchi, I.; Aurian-Blajeni, B.; Bockris, J. O'M. *Electrochim. Acta* **1984**, *29*, 923.

(24) Zafrir, M.; Ulman, M.; Zuckerman, Y.; Halmann, M. *J. Electroanal. Chem.* **1983**, *159*, 373.

(25) Canfield, D.; Frese, K. W., Jr. *J. Electrochem. Soc.*, **1983**, *130*, 1772.

(26) Meshitsuka, S.; Ichikawa, M.; Tamaru, K. *Chem. Commun.* **1974**, 158.

(27) Hiratsuka, K.; Takahashi, K.; Sasaki, H.; Toshima, S. *Chem. Lett.* **1977**, 1137.

(28) Takahashi, K.; Hiratsuka, K.; Sasaki, H.; Toshima, S. *Chem. Lett.* **1979**, 305.

(29) Fischer, B.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 7363.

(30) Kapusta, S.; Hackerman, N. *J. Electrochem. Soc.* **1984**, *131*, 1511.

(31) Lieber, C. M.; Lewis, N. S. *J. Am. Chem. Soc.* **1984**, *106*, 5033.

(32) Bradley, M. G.; Tysak. T.; Graves, D. J.; Vlachopoulos, N. A. *Chem. Commun.* **1983**, 349.

(33) Tinnemans, A. H. A.; Koster, T. P. M.; Thewissen, D. H. M. W.; Mackor, A. M. *Recl. Trav. Chim. Pays-Bas* **1984**, *103*, 288.

(34) Tezuka, M.; Yajima, T.; Tsuchiya, A.; Matsumoto, Y.; Uchida, Y.; Hidai, J. *J. Am. Chem. Soc.* **1982**, *104*, 6834.

(35) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *Chem. Commun.* **1984**, 328.

(36) Slater, S.; Wagenknecht, J. *J. Am. Chem. Soc.* **1984**, *106*, 5367.

(37) Bolinger, C. M.; Sullivan, B. P.; Conrad, D.; Gilbert, J. A.; Story, N.; Meyer, T. J. *Chem. Commun.* **1985**, 96.

(38) Stalder, C. J.; Chao, S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 3673.

(39) Parkinson, B. A.; Weaver, P. F. *Nature* (*London*) **1984**, *309*, 148.

(40) Lehn, J.-M.; Ziessel, R. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 701.

(41) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *Chem. Commun.* **1983**, 536.

(42) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *Chem. Commun.* **1985**, 56.

(43) Beley, M.; Collin, J.-P.; Ruppert, R.; Sauvage, J.-P. *Chem. Commun.* **1984**, 1315.

(44) Bush, D. H. *Acc. Chem. Res.* **1978**, *11*, 392.

(45) Bosnich, B.; Tobe, M. L.; Webb, G. A. *Inorg. Chem.* **1965**, *4*, 1102, 1109.

(46) Grant, W. M. *Anal. Chem.* **1948**, *20*, 267.

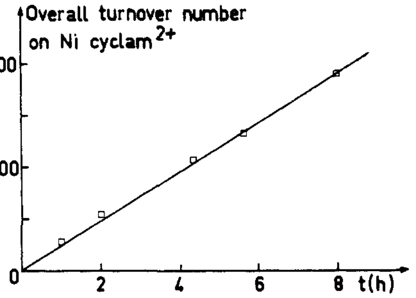


Figure 1. Overall turnover number on Ni cyclam^{2+} (mol of CO produced/mol of nickel complex introduced) as a function of electrolysis time. Experimental conditions: [Ni cyclam^{2+}] = 1.7 × 10^{-6} M; 25 mL of 0.1 M $KClO_4$ at pH 4.1; 20 °C, 1 atm of CO_2; mercury cathode; applied potential −1.00 V vs. NHE.

Table II. Amount of CO Generated in 4 h of Electrolysis as a Function of [Ni cyclam^{2+}]^a

[Ni cyclam^{2+}] (M)	CO prodcd in mL	turnover freq^b
3.3 × 10^{-4}	25.6	14 (46)
1.0 × 10^{-4}	29.5	47 (165)
5 × 10^{-5}	24.0	82 (265)
1.0 × 10^{-5}	13.5	198 (750)
3.3 × 10^{-6}	7.5	330 (1250)

^{a}Same experimental conditions as in Table I except for the support electrolyte which is now 0.1 M $KClO_4$; applied potential: −1.00 V vs. NHE. ^{b}Overall turnover after 4 h is in parentheses.

pied by gases. Before electrolysis, the aqueous solution (75 mL) was degassed by bubbling CO_2 through it for 30 min, after which the admission tap was turned off, the internal pressure within the electrolysis cell being kept equal to 1 atm by means of an oil valve. Turnover frequencies are calculated as mol of CO produced per mol of electrocatalyst introduced in 1 h.

Cyclic voltammograms (scan rate: 20–1000 mV·s^{-1}) were carried out in a standard cell (Metrohm) by using a Bruker E 130 M potentiostat. A hanging mercury electrode (Kemula type: drop surface = 1.8 mm^2) was used as working electrode. The intensity-potential curves were obtained in freshly prepared buffer solutions (potassium phosphate) or in nonbuffered solutions (potassium perchlorate or nitrate). The pH was continually measured during the experiment and adjusted if necessary with a small volume of concentrated acid or base.

Results and Discussion

(1) Electrolysis of CO_2 Saturated Aqueous Solutions in the Presence of Ni Cyclam^{2+}: Experimental Data. The behavior of Ni cyclam^{2+} as an electrocatalyst for reduction of CO_2 was unique among the numerous complexes investigated (Fe^{II}, Co^{II} or Ni^{II} complexes of cyclic or acyclic nitrogen containing ligands). At potentials as low as −0.9 V vs. NHE, CO_2 was selectively reduced to CO even in water. Some typical experimental results are collected in Table I.

The velocity of the reaction is remarkable, the turnover frequency of Ni cyclam^{2+} being 32 h^{-1} at a potential of −1.05 V. Even more interesting is the selectivity of the process, the faradaic yield being quantitative within experimental error when the cathodic potential is −1.0 V or more negative. Under the experimental conditions of Table I, no hydrogen could be detected in the gas generated during the reaction, despite the very sensitive chromatographic analysis method (see Experimental Section). For experiment number 5, the H_2 to CO ratio is smaller than 0.03%. Taking account of the respective concentrations of H_2O (55 mol·L^{-1}) and CO_2 (0.1 mol·L^{-1}) in the medium, the actual selectivity for reduction of CO_2 vs. that of H_2O is higher than 10^6.

In order to estimate the stability of the electrocatalyst and to determine the influence of the Ni cyclam^{2+} concentration on the rate of CO_2 reduction, we performed a series of experiments with variable amounts of electrocatalyst, the least concentrated systems being studied as a function of time.

The experimental results are shown in Table II and Figure 1. Two main points should be noted. Firstly the influence of the catalyst concentration on the velocity of CO generation is not very important. For example, increasing the Ni cyclam^{2+} concentration 100-fold leads to an increase in rate of CO formation by a factor of only 3. This is a good indication that the concentration of Ni cyclam^{2+} in the bulk is not rate determining, but that on the contrary, interface reactions are very important. Secondly the stability of the electrocatalytic system is excellent, as shown in Figure 1. After 8000 turnovers (8 h of electrolysis), the catalytic activity remains intact. The efficiency of the process is also remarkable, the turnover frequency being 1000 h^{-1} under the conditions given in Table I (at 20 °C with an applied potential of −1.0 V). Except in acidic medium, we have never observed decomposition of the electrocatalyst.

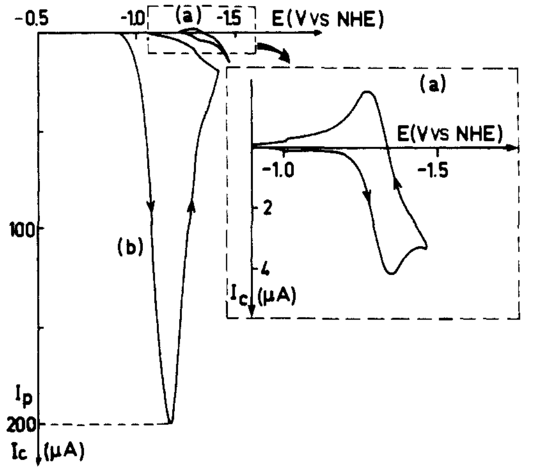


Figure 2. Intensity–potential curves for Ni cyclam^{2+} (10^{-3} M) in 0.1 M $KClO_4$ (pH 4.5) under N_2 (curve a) or CO_2 (curve b); hanging mercury electrode; scan rate 100 mV·s^{-1}.

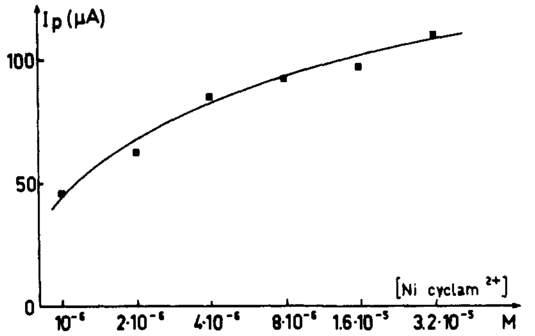


Figure 3. Variation of the peak intensity I_p as a function of [Ni cyclam^{2+}] under CO_2; same experimental conditions as in Figure 2.

(2) Mechanistic Investigation. (a) Study of the Electrocatalytic Nature of the Process by Cyclic Voltammetry. Cyclic voltammograms of Ni cyclam^{2+} in aqueous solution, under N_2 or CO_2, are shown in Figure 2. In the absence of CO_2, the Ni cyclam^{2+}/Ni cyclam$^+$ couple is reversible in water ($KClO_4$ as supporting electrolyte), as shown by curve a, the redox potential being $E° = -1.33$ V vs. NHE. Under CO_2 (curve b), reversibility is completely lost. However, a catalytic wave is observed having the following properties: (i) an important shift toward anodic potentials (300 mV) with respect to the corresponding wave under nitrogen and (ii) a high peak intensity, as compared to that measured for other electrocatalysts investigated. This peak intensity is several orders of magnitude greater than that obtained under N_2 (10^4 for [Ni cyclam^{2+}] = 10^{-6} M), indicating a particularly efficient electrocatalytic process.

Cyclic voltammograms were recorded at various concentrations of the nickel complex. Under CO_2, the catalytic wave is still observed even for very low concentrations. The variation of the peak intensity vs. [Ni cyclam^{2+}] is represented in Figure 3. Remarkably, the intensity I_p is only weakly dependent on the concentration of the nickel complex. I_p is only doubled when [Ni cyclam^{2+}] is increased by a factor of 30. Again, these observations strongly support the importance of adsorbed species as compared

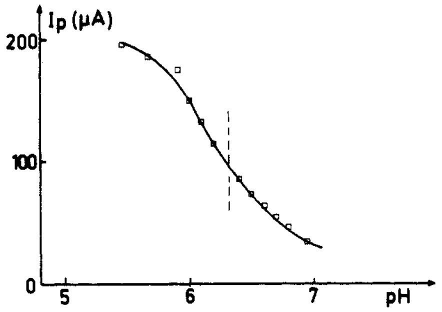


Figure 4. Influence of the pH. Variation of the peak intensity as measured under the experimental conditions of Figure 2, the pH being adjusted by gradual addition of concentrated KOH.

to those contained in the bulk. This is in agreement with electrolysis experiments carried out on dilute Ni cyclam^{2+} solutions (vide supra).

(b) CO_2 as a Substrate. Acid–base equilibria involving CO_2, HCO_3^-, or CO_3^{2-} must be taken into account because the reduction of CO_2 to CO (1) involves protons. The efficiency of Ni cyclam^{2+}

$$CO_2 + 2e^- + 2H^+ \rightarrow CO + H_2O \qquad E° = -0.52V \quad (1)$$

$$CO_2 + H_2O \rightarrow HCO_3^- + H^+ \qquad pK_{a1} = 6.37 \quad (2)$$

$$HCO_3^- + H_2O \rightarrow CO_3^{2-} + H^+ \qquad pK_{a2} = 10.37 \quad (3)$$

in electrocatalysis has been studied as a function of pH, in order to determine if the system depends on the acid–base equilibria (2) and (3). We found by either (i) continuous electrolysis or (ii) cyclic voltammetry that CO is formed exclusively via reduction of the dissolved carbon dioxide and that HCO_3^- or CO_3^{2-} are not precursors for the generation of CO. Indeed, the peak current intensity of Ni cyclam^{2+} reduction in the presence of CO_2 shows a linear variation as a function of CO_2 concentration in the range 0.86×10^{-2}–3.47×10^{-2} M.

(i) Electrolysis performed in a potassium carbonate buffer ($KHCO_3/K_2CO_3$; 0.25 M; pH 10.6) leads mainly to hydrogen generation with only traces of CO. However, in acidic media using phosphate buffers, H_2 is detected, the efficiency of CO production being only slightly altered. For example, at pH 4 (potassium phosphate buffer; 0.2 M) the current efficiency for H_2 generation reaches 0.3%. At lower pH, the reduction of H_2O (or H^+) competes more effectively with reduction of CO_2. This could be due to either the effect of the H^+/CO_2 ratio or to decomposition of the electrocatalyst. In the latter case free nickel would be produced, catalyzing the formation of H_2 (see Table I).

(ii) A series of voltammograms was recorded at various pH values. Figure 4 represents the variation of I_p as a function of pH. The I_p/pH dependence is probably due to acid–base equilibria, involving protonation of bound CO_2 on a reduced complex or its reduction products. The nature of the anion of the support electrolyte also has an influence on the course of the electrocatalytic reaction. Using KNO_3 or $KClO_4$, H_2 is not detected at pH 4. The use of phosphate or tetrafluoroborate (KH_2PO_4, KBF_4) decreases the selectivity of the process. This phenomenon is probably related to the reduction of the anion itself, preventing H_2 formation when reduced nickel species escape the CO_2 electrocatalytic cycle.

Cyclic voltammetry experiments conducted in the presence of increasing amounts of KNO_3 clearly show a catalytic wave corresponding to reduction of the nitrate ion. This electrocatalytic process is efficient even at a high scan rate. Electrolysis of a KNO_3 solution in the presence of Ni cyclam^{2+}, at −1.0 V and under a methane atmosphere, leads to formation of nitrite and other products. The sole participation of CO_2 as a reducible substrate, as opposed to its corresponding bases HCO_3^- and CO_3^{2-}, is corroborated by the effect of temperature on the efficiency of the system, as represented in Figure 5a. For convenience, the variation of CO_2 solubility in water as a function of temperature is also indicated (Figure 5b). The turnover frequency (CO produced/Ni cyclam^{2+} introduced, per hour) reaches a maximum

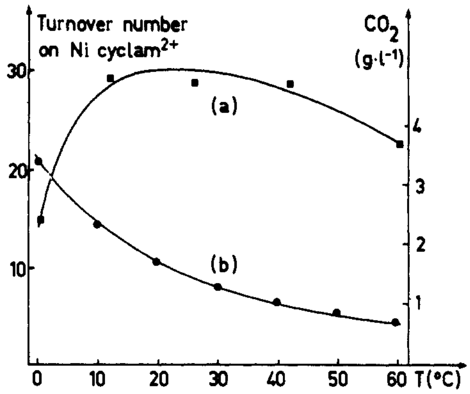


Figure 5. Activity of the electrocatalyst (mercury pool cathode; applied potential −1.05 V vs. NHE; 0.1 M KNO_3; ([Ni cyclam^{2+}] = 1.5×10^{-4} M) as a function of temperature (curve 5a) and variation of CO_2 solubility (curve 5b).

at about room temperature. Above 20 °C, the observed decrease in reaction rate is most likely due to the lower solubility of CO_2. The shape of the curve (Figure 5a) reflects a balance between the rate constants of the chemical and electrochemical reactions and the solubility of CO_2, the latter being rate determining above room temperature. H_2 is produced above 50 °C, although the selectivity for CO_2 reduction remains relatively high (at 60 °C, the faradaic yield for H_2 generation is $\sim$1%).

(c) Importance of the Adsorbed Species. In order to estimate the relative contributions of the adsorbed species and those in solution, we have studied the reaction between nickel(I) complexes and CO_2. Unfortunately, all our attempts to generate Ni^{I} cyclam$^+$ in water, either electrochemically or by chemical reduction (sodium amalgam), gave negative results. Ni^{I} cyclam$^+$ reacts rapidly with H^+ in contrast with nickel complexes of N- or N- and C-methylated ligands, whose monovalent state is relatively stable in aqueous media.[47] Ni^{I} cyclam$^+$ may only be observed as a transient species by pulse radiolysis spectroscopy.[48] However, Ni^{I} cyclam$^+$ is easily prepared in anhydrous media and its reaction with CO_2 will be discussed later. The presence of adsorbed species under N_2 and particularly under CO_2 was determined by cyclic voltammetry and by polarography. The intensity-potential curves obtained with CO_2-saturated solutions of Ni cyclam^{2+} are not very informative from a mechanistic viewpoint. However, interesting observations may be made if only small amounts of CO_2 are introduced, the Ni^{II}/CO_2 stoichiometry being kept in the range of 1. The voltammograms measured are represented in Figure 6. Under N_2 (Figure 6a) the Ni^{II} cyclam^{2+}/Ni^{I} cyclam$^+$ couple is reversible. Of note is the presence of a prewave at approximately −1.25 V vs. SCE. This phenomenon may result from the adsorption of the reduced complex, Ni^{I} cyclam$^+$, on the mercury electrode.[49] The same type of prewave is also observed by polarography, and this could not be eliminated by the use of surfactants (triton X 100, for example). Under CO_2 (Figure 6b) two irreversible waves are detected at −1.35 and −1.44 V vs. SCE, the reversible Ni^{II} cyclam^{2+}/Ni^{I} cyclam$^+$ couple being observed at −1.57 V vs. SCE. The two irreversible prewaves correspond to the catalytic wave which occurs in CO_2 saturated solution (Figure 2b). They are observed at the same potential as the adsorption prewave.

The anodic shift (by 300 mV) of the Ni cyclam^{2+} reduction wave under CO_2 may be explained as follows. The reduced complex Ni^{I} cyclam$^+$ is strongly adsorbed on the electrode (Figure 6a). The adsorbed species interacts with CO_2, the reduction of coordinated CO_2 taking place mainly on the electrode surface. Such a phenomenon would explain the saturation effect observed

---

[47] Jubran, N.; Ginzburg, G.; Cohen, H.; Meyerstein, D. *Chem. Commun.* **1982**, 517.

[48] Jubran, N.; Ginzburg, G.; Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1985**, *24*, 251.

[49] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Application*; Wiley: 1980; Chapter 12.

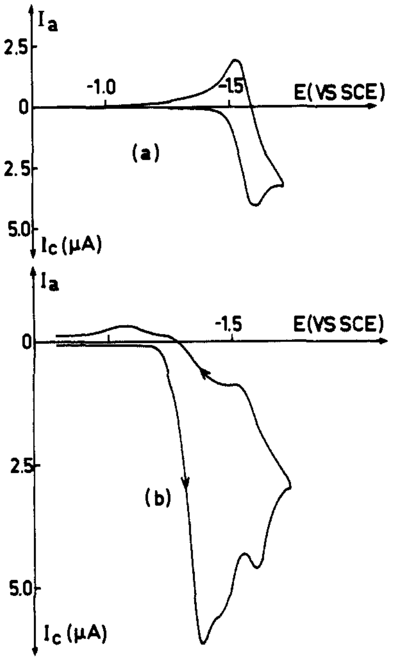


Figure 6. Cyclic voltammograms of Ni cyclam^{2+} (10^{-3} M) in 0.1 M $KClO_4$ (pH 5) (a) under N_2 and (b) in the presence of a small amount of CO_2.

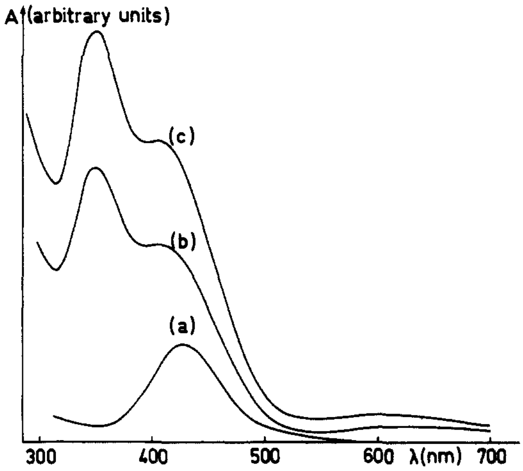


Figure 7. UV–vis spectroscopy study in aqueous solution. (a) Electronic spectrum of Ni cyclam^{2+} before electrolysis. (b) Electronic spectrum of Ni cyclam^{2+} electrolyzed under 1 atm of CO_2. (c) Electronic spectrum of Ni cyclam^{2+} electrolyzed under 1 atm of CO. Experimental conditions: [Ni cyclam^{2+}] = 7.5×10^{-3} M in 0.1 M aqueous $KClO_4$ at 20 °C; electrolysis, Hg pool at −1.00 V vs. NHE.

by increasing the electrocatalyst concentration (see Figure 3), reactions occurring in the bulk being of only minor importance.

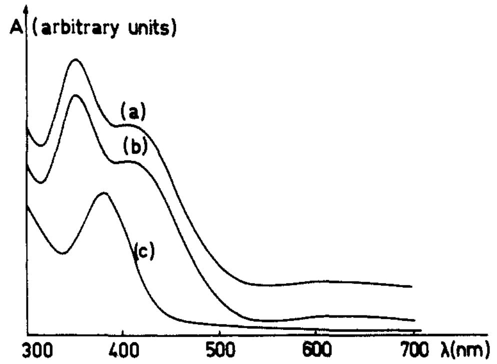


Figure 8. Electronic spectra of electroreduced (mercury cathode; −1.45 V vs. SCE) Ni cyclam^{2+} in DMF (0.1 M NBu_4BF_4) (a) under CO_2, (b) under CO, and (c) under N_2. Curves a and b correspond to the same species: Ni (cyclam)(CO)$^+$.

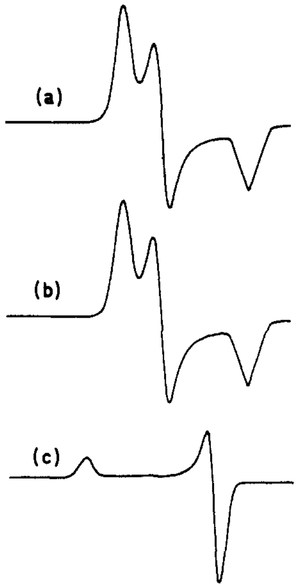


Figure 9. EPR spectra of frozen (77 K) electrolyzed solutions of Ni cyclam^{2+} in DMF (electrolysis conditions as in Figure 8) (a) under CO_2, (b) under CO, and (c) under N_2.

(d) Are Nickel(I) Carbonyl Complexes Intermediates in the Electrocatalytic Cycle? Several methods have been used in an attempt to identify the intermediates present during the electrocatalytic process. During the course of electrolysis under CO_2, the initial yellow color of the solution (absorption maximum λ_{max} = 450 nm) becomes yellow-green. The electronic spectrum of a solution during electrolysis is represented in Figure 7. This spectrum does not correspond to that of Ni cyclam$^+$, the latter being observed only as a transient species in aqueous medium[48] (λ_{max} = 375 nm; extinction coefficient ϵ = 4500). At present, the nature of the green species observed under CO_2 during electrolysis is unknown. However, it is reasonable to suggest the formation of nickel(I) carbonyl complexes. In fact identical reduced species are formed by electrolysis under CO_2 or under CO. The electronic spectra of the two reduced complexes are almost superimposable, as shown in Figure 7. In addition, the EPR spectra of frozen electrolyzed solutions under CO or under CO_2 show the same signal at $g = 2.120$. The participation of carbonylated complexes might also be postulated on the basis of further studies carried out in anhydrous media as discussed below. Under nitrogen, Ni cyclam$^+$ is readily generated electrochemically in dimethylformamide (DMF), at a potential of −1.4 V vs. SCE. Such macrocyclic nickel(I) complexes have been observed previously by others[50–58] following the pioneering work of Olson and Vasilevskis.[50] The electronic spectrum of Ni cyclam$^+$ in DMF is shown in Figure 8. It is in agreement with that measured by others in H_2O[48] and is similar to those of analogous macrocyclic nickel(I) complexes in acetonitrile.[50] Interestingly, electrolysis of Ni cyclam^{2+} in DMF, either under CO or under CO_2 gives identical species (see Figure 8). The same phenomenon may also be demonstrated by EPR spectroscopy, as represented in Figure 9. In DMF under N_2, Ni^I cyclam$^+$ shows an EPR spectrum ($g_1\perp = 2.047$, $g\parallel = 2.258$) close

---

(50) Olson, D. C.; Vasilevskis, J. *Inorg. Chem.* **1969**, *8*, 1611.

(51) Rillema, D. P.; Endicott, J. F.; Papacontantinou, E. *Inorg. Chem.* **1971**, *10*, 1739.

(52) Lovecchio, F. V.; Gore, E. S.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 3109.

(53) Tait, A. M.; Hoffman, M. Z.; Hayon, E. *Inorg. Chem.* **1976**, *15*, 934.

(54) Becker, J. Y.; Kerr, J. B.; Pletcher, D.; Rosas, R. *J. Electroanal. Chem.* **1981**, *117*, 87.

(55) Ansell, C. W. G.; Lewis, J.; Raithby, P. R.; Ramsden, J. N.; Schröder, M. *Chem. Commun.* **1982**, 546.

(56) Constable, E. C.; Lewis, J.; Schröder, M. *Polyhedron* **1982**, *1*, 311.

(57) Constable, E. C.; Lewis, J.; Liptrot, M. C.; Raithby, P. R.; Schröder, M. *Polyhedron* **1983**, *2*, 301.

(58) Dietrich-Buchecker, C. O.; Kern, J.-M.; Sauvage, J.-P. *Chem. Commun.* **1985**, 760.

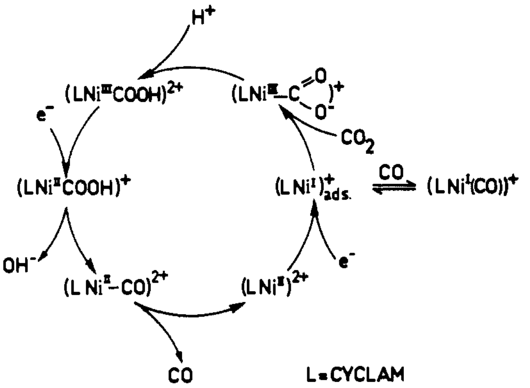


Figure 10. Postulated mechanistic cycle for the electrocatalytic reduction of CO_2 into CO by Ni cyclam^{2+} in water.

to that reported earlier in CH_3CN.[54] Under CO or CO_2 the EPR spectrum has three signals at $g_1 = 2.196$, $g_2 = 2.137$, and $g_3 = 2.017$. Such a spectrum is characteristic of a C_{4v} pentacoordinated d^9 nickel(I) complex.[59,60] Several tetraazamacrocyclic complexes of Ni^I, having carbonyl as a fifth ligand and with a square-pyramidal geometry; have been generated in solution,[60] and these display EPR spectra (propylene carbonate glasses at 100 K) very similar to that of Figure 9. This strongly suggests that the compound obtained in DMF is $Ni^I(cyclam)(CO)^+$. It is noteworthy that under CO_2, this 19-electron d^9 complex corresponds to a three-electron reduction product from Ni cyclam^{2+} and CO_2

$$\text{Ni cyclam}^{2+} + CO_2 + 2H^+ + 3e^- \rightarrow \text{Ni(cyclam)(CO)}^+ + H_2O$$

On the other hand, its formation under CO is straightforward

$$\text{Ni cyclam}^{2+} + e^- \rightarrow \text{Ni cyclam}^+$$

$$\text{Ni cyclam}^+ + CO \rightarrow \text{Ni(cyclam)(CO)}^+$$

The infra-red spectrum in solution (DMF; 10^{-2} M of nickel complex) of the reduction product of Ni cyclam^{2+} under CO or CO_2 also supports the formation of $Ni(cyclam)(CO)^+$. A sharp peak is observed at 1945 cm^{-1}, typical of a coordinated CO stretching vibration.

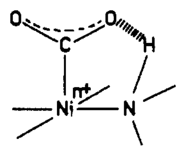
Although the chemical species generated during electrolysis of Ni cyclam^{2+} (under CO or CO_2) in H_2O and in anhydrous DMF have similarities, their spectroscopic properties are not identical. The difference in aqueous solutions may arise from coordination of H_2O to the nickel atom or reaction of the coordinated CO with H_2O (or OH^-) to form a metallocarboxylic acid (or carboxylate). Clearly, the nickel(I) carbonyl complex is much more stable in DMF than in H_2O, allowing its characterization in the former medium. The instability of $Ni(cyclam)(CO)^+$—or its aquation product—may be responsible for the efficiency of the electrocatalytic process in water, fast decomposition of this intermediate with liberation of CO providing rapid regeneration of the catalyst.

(e) Proposed Mechanistic Scheme. The initial step is probably reduction of the nickel(II) complex, the nickel(I) product being strongly adsorbed on the electrode surface. The latter (Ni cyclam$^+$) might either interact with a proton to form a Ni^{III} hydride or react with CO_2. The postulated catalytic cycle is represented in Figure 10. The formation of a nickel hydride according to

$$Ni^I \text{ cyclam}^+ + H_2O \rightarrow H\text{-}Ni^{III} \text{ cyclam}^{2+} + OH^-$$

is unlikely since, although hydrides are precursors for hydrogen formation, no H_2 is detected. On the other hand, small amounts of H_2 are detected if CO_2 is omitted. As indicated in Figure 10, CO_2 interacts with Ni cyclam$^+$, this reaction being favored if the nickel(I) species is adsorbed on the electrode. The nickel(III) complex obtained should easily be protonated and reduced, the nickel(II) carbonyl complex thus formed being only weakly bound to CO. After CO expulsion, the starting nickel(II) compound is regenerated. After a few cycles, CO is present in the electrolysis cell. As a consequence, several of the catalytic species in the scheme (Figure 10) may be in equilibrium with their carbonylated analogues, as is the case for Ni^I cyclam$^+$. Such equilibria might be important in the process since the CO complexes thus obtained might be electroreduced more easily than the corresponding noncarbonylated species.

Chart I



(3) Factors Related to the Exceptional Efficiency and Selectivity of Ni Cyclam^{2+} as an Electrocatalyst. The replacement of Ni cyclam^{2+} by other related nickel(II) complexes in the present electrocatalytic system was disappointing. The use of unsaturated or methylated tetraaza 14-membered rings as ligands was previously shown to affect CO/H_2 selectivity.[29,32] In addition, tetraaza open chain ligands or macrocyclic ligands other than cyclam (14 atoms in the ring) show poor stability during the electroreductive process.

The efficiency and stability of the Ni cyclam^{2+} based electrocatalytic system are probably due to the kinetic inertness of cyclam complexes as compared to other acyclic or cyclic compounds. When dissolved in acidic medium, Ni cyclam^{2+} is not decomplexed even after several months whereas the 13- or 15-membered ring complexes are rapidly dissociated (within hours).[44] Acyclic ligands give even more labile complexes, as demonstrated for various transition-metal complexes, the phenomenon being known as the "macrocyclic effect".[61] At present, the reasons for the exceptional selectivity are still speculative. Interestingly, steric factors seem to play an important role. Introduction of methyl groups at the periphery of the complex drastically decreases the CO to H_2 ratio in the gas produced. A relatively unhindered Ni cyclam$^+$ species is likely to react preferentially with CO_2 rather than with H^+, the former substrate being much larger than the latter. On the other hand, a nickel(I) complex whose metal center is hindered by substituents borne by the ligand will certainly react faster with H^+ than with CO_2. It is also tempting to invoke the formation of a hydrogen-bonded CO_2 complex when the coordinating sites are secondary amines. The accessibility of Ni^I and the presence of N–H functions in Ni cyclam$^+$ could favor the formation of a CO_2 complex, the substrate being bound on two sites, as represented in Chart I. The binding of CO_2 via both its electrophilic center (carbon atom) and basic site (oxygen atom) is reasonable. Indeed, it has recently been shown that bifunctional complexation of CO_2 is possible, the carbon atom being bound to a cobalt(I) center and the oxygen atoms interacting with a Lewis acid such as Na^+ or K^+.[62-65] In the case of Ni cyclam^{2+}, it has been postulated on the basis of X-ray crystallography that there is electrostatic repulsion between the N–H hydrogen atoms and water molecules.[45] This supports the stabilization of a bound CO_2 by interaction with the acidic hydrogen borne by the secondary amine.

Conclusion

In conclusion, we have shown that Ni cyclam^{2+} is a highly efficient and selective electrocatalyst for reduction of CO_2 to CO. The process is remarkably fast at potentials as accessible as −1.00

---

(59) Gagné, R. R.; Ingle, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 1444.

(60) Gagné, R. R.; Ingle, D. M. *Inorg. Chem.* **1981**, *20*, 420.

(61) Cabbiness, D. K.; Margerum, D. W. *J. Am. Chem. Soc.* **1970**, *92*, 2151.

(62) Fachinetti, G.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1978**, *100*, 7405.

(63) Fachinetti, G.; Floriani, C.; Zanazzi, P. F.; Zanzari, A. R. *Inorg. Chem.* **1978**, *18*, 3469.

(64) Gambarotta, S.; Arena, F.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1982**, *104*, 5082.

(65) Bianchini, C.; Meli, A. *J. Am. Chem. Soc.* **1984**, *106*, 2698.

J. Am. Chem. Soc. **1986**, *108*, 7467–7477

V vs. NHE (turnover frequency ~10^3 mol of CO produced per mol of nickel complex, in 1 h) and selective, even in a purely aqueous medium. The stability of the complex used makes it a promising electrocatalyst (10^4 electrocatalytic cycles on Ni cyclam^{2+} without degradation). In the present study, we have detected a nickel(I) carbonyl complex which may participate in the catalytic cycle. Other important reaction parameters have been investigated. The efficiency of Ni cyclam^{2+} in the electroreduction of CO_2 may be due to the size of the cyclam ring (14 atoms), which greatly stabilizes nickel complexes. A reason for the selectivity of the electrocatalyst may be difunctional activation of CO_2. The acidic character of the N–H protons of cyclam could favor CO_2 fixation by hydrogen bonding (N–H···O) in addition to the carbon to nickel(I) link.

Acknowledgment. This research was supported by the CNRS (PIRSEM). We also thank the financial contribution of the Agence Française pour la Maîtrise de l'Energie.

Theoretical Determination of Molecular Structure and Conformation. 20. Reevaluation of the Strain Energies of Cyclopropane and Cyclobutane—CC and CH Bond Energies, 1,3 Interactions, and σ-Aromaticity

Dieter Cremer* and Jürgen Gauss

Contribution from the Lehrstuhl für Theoretische Chemie, D-5000 Köln 41, West Germany.
Received April 22, 1986

Abstract: In order to rationalize the striking similarity of the strain energies (SE) of cyclopropane (**1**, 28 kcal/mol) and cyclobutane (**2**, 27 kcal/mol), the energetic consequences of Pitzer strain, Baeyer strain, hybridization effects (CH bond strengthening), Dunitz–Schomaker strain (1,3 CC interactions), and bond stretching effects have been quantitatively assessed at the HF/6-31G** level of theory. Calculations have been based on chemically meaningful definitions of bond length, bond angle, bond energy, and bending force constant in strained molecules. Results reveal that Pitzer strain in both **1** and **2** is just 4 kcal/mol and that CH bond strengthening stabilizes **1** by 6 kcal/mol (**2** by 3 kcal/mol), far less than has been assumed previously. The calculated Baeyer strain of **1** and **2** is 41 and 13 kcal/mol, respectively. SE(**1**) and SE(**2**) can only be compared if a correction term of 9 kcal/mol due to Dunitz–Schomaker strain (present in **2**, but absent in **1**) is taken into account. The analysis of the various energy contributions to the SEs of **1** and **2** reveals that **1** is stabilized by at least 17 kcal/mol. Both MO and electron density analysis suggest that **1** is totally different from the other cycloalkanes in being stabilized by 3-center 2-electron delocalization. σ-Electrons are delocalized in the surface of the three-membered ring, a phenomenon which may be described by the term σ-aromaticity. The concept of σ-aromaticity helps to rationalize the unusual properties of **1**, the changes in the stability of **1** upon substitution, the stability of sila and germa analogues of **1** and **2**, as well as the properties of bi- and tricyclic compounds containing **1** and **2** as subunits.

(I) Introduction

It is a puzzling observation that the conventional ring strain energies (CRSE) of cyclopropane (**1**, 27.5 kcal/mol) and cyclobutane (**2**, 26.5 kcal/mol) are almost the same.[1,2] According to the classical definition of strain introduced by Baeyer more than a century ago,[3] the three-membered ring should be clearly more strained than the four-membered ring. Its bond angles deviate from the standard, strain-free CCC angle (109.5°) by $\Delta\alpha = 49.5°$ while those of a planar four-membered ring deviate just by 19.5°. Assuming that bond angle strain $\Delta E(\mathrm{B})$ (Baeyer strain) increases with the square of $\Delta\alpha$ according to

$$\Delta E(\mathrm{B}) = n\frac{k_\alpha}{2}(\Delta\alpha)^2 \qquad \text{(I)}$$

(n, size of ring; k_α, CCC bending force constant), Baeyer strain of **1** should be 5 times as high as that of **2**. Utilizing k_α of propane (**3**) (1.071 mdyn·Å/rad^2)[4] the Baeyer strain of **1** and **2** is calculated to be 173 (!) and 36 kcal/mol, respectively. These values suggest (a) that the difference in the CRSE values of **1** and **2** should be larger than observed and (b) that it may be too simple-minded to use geometrical angles α and k_α of **3** to evaluate $\Delta E(\mathrm{B})$: The CRSE of **2** is just 26.5 kcal/mol[1] and a difference of more than 130 kcal/mol between the $\Delta E(\mathrm{B})$ values of **1** and **2** is certainly too large. Nevertheless, Baeyer strain of **1** should be considerably larger than that of **2** and, therefore, the similarity of the CRSE values is unexpected, a fact which for a long time has been disguised by discussing strain energies per CH_2 group (9.2 kcal/mol for **1** and 6.6 kcal/mol for **2**) rather than total CRSE values.

In principle, there are two different explanations possible for the striking anomaly in the CRSE of **1** and **2**. On the one hand, the experimentally found CRSE of **1** could signal a stabilizing effect which reduces the actual Baeyer strain of **1**. This would mean that the CRSE of **2** is normal. On the other hand, the CRSE of **2** could be abnormally high while that of **1** is normal.

Both explanations have been aired, and a number of electronic effects adding to the Baeyer strain of **1** and **2** have been invoked[5–9] to rationalize the magnitudes of CRSE (**1**) and CRSE (**2**). These are torsional strain (Pitzer strain),[2] rehybridization effects (CH bond strenghtening),[5] nonbonded interactions (Dunitz–Schomaker strain),[6,7] and effects arising from σ-electron delocalization.[8–10]

---

[1] (a) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic: London, 1970. (b) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976.

[2] (a) Ferguson, L. N. *Highlights of Alicyclic Chemistry*; Franklin: Palisades, NJ, 1973; Part 1, Chapter 3. (b) Greenberg, A.; Liebman, J. *Strained Organic Molecules*; Academic: New York, 1978 and references cited. See also: (c) Charton, M. In *The Chemistry of Alkenes*; Zabicky, J., Ed.; Wiley-Interscience: New York, 1970; Vol. 2. (d) Wendisch, D. In *Methoden der Organischen Chemie*; Houben-Weyl-Müller; Thieme Verlag: Stuttgart, 1971; Vol. IV, p 3. (e) Schleyer, P. v. R.; Williams, J. E., Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377–2386. (f) Wiberg, K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312–322.

[3] Baeyer, A. *Chem. Ber.* **1885**, *18*, 2269–2281. See also: Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 297–311.

[4] (a) Snyder, R. G.; Schachtschneider, J. M. *Spectrochim. Acta* **1965**, *21*, 169–195. (b) Snyder, R. G.; Zerbi, G. *Spectrochim. Acta* **1967**, *23A*, 391–437.

[5] Coulson, C. A.; Moffitt, W. E. *Phil. Mag.* **1949**, *40*, 1–35.

0002-7863/86/1508-7467$01.50/0