at C3′ and C2′, and the base at C1′) on all four of the sugar-ring carbons upon passing from one conformer to another.

Summary

Evidence has been presented that the sugar pucker (^3E) and the phosphate ring conformation for a six-membered phosphate ring fused cis 1,2 to a five-membered sugar ring are both invariant to the nature of the β-C1′ substituent and the epimeric orientation of a hydroxyl group at C2′. Similarly, for a seven-membered phosphate ring fused cis 1,3 to a five-membered pentose sugar, the sugar pucker (^2E) and the phosphate ring conformation are both invariant to the nature of the β-C1′ substituent and to the epimeric orientation of a hydroxyl group at C3′. However, in this same bicyclic ring system, release of the unfavorable steric interactions between the base and the phosphate ring, by transposition of the base to the α-configuration, causes a change in the phosphate ring conformation to a more energetically favored chair form, whereas the sugar pucker remains invariant (^2E). The conformational information from the NMR data has permitted unequivocal identification of the cyclic 2′,5′- and 3′,5′-monophosphates of lyxouridine for the first time and, in addition, has provided a rational mechanistic explanation for the isomerization of the 2′,5′-isomer to the 3′,5′-isomer. In the light of the analyses for these conformationally fixed cyclic phosphates, a reevaluation of the coupling data for the free nucleosides lyxouridine and lyxoadenosine indicates that they exist in solution at ambient temperature either in a $^3E/^3_4T$ or a $_3E/^4_3T$ conformation (or in an equilibrium between these two conformers), in contrast to a previous interpretation of the NMR data.

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Communications to the Editor

Electrocatalytic Reduction of Carbon Dioxide by Using Macrocycles of Nickel and Cobalt

Sir:

The reduction of carbon dioxide, this planet's most abundant source of carbon, is an important objective in the development of alternative fuel sources. This reduction requires both the action of a catalyst and energy input to be viable. The former is a result of the large overpotential associated with the direct electrochemical reduction of CO_2, while the latter results from the fact that CO_2 is the stable carbon end product of metabolism and other combustions. Equation 1 shows the half-cell reaction for the two-

$$CO_2 + 2e^- + 2H^+ = CO + H_2O \qquad (1)$$

electron reduction of CO_2 to CO. The standard potential for this reaction is −0.10 V while at pH 7 the potential becomes −0.52 V. The direct electroreduction of CO_2 on various metal electrodes in both aqueous and nonaqueous media has been reported by numerous authors.[1-4] However, these direct electroreductions have required potentials more negative than ca. −2 V vs. SCE. In this paper, we describe an *indirect* electrochemical reduction of CO_2 which involves the initial reduction of metal complexes and their subsequent reaction with CO_2. This approach facilitates reducing CO_2 at potentials closer to the thermodynamic values. The metal complexes are thus redox-activated catalysts.

The catalysts employed were the tetraazamacrocyclic complexes (**1**–**5**) of cobalt and nickel. These are listed in Table I, along with the cell potentials applied during the electrocatalytic reactions. The preparation and electrochemical behavior of these complexes in nonaqueous solvents have been previously reported.[5] Each complex undergoes uncomplicated reversible or quasi-reversible one-electron transfers in dry, nonaqueous solvents. Evidence for CO_2 reduction was obtained from controlled potential coulometry (cpc) experiments performed in a gas-tight electrolysis cell under an exclusively carbon dioxide atomosphere.[6] The concentration of catalyst ranged from 1 to 2.5 mM in these experiments, and the solvent systems used were either acetonitrile/water or water only. Gas chromatographic analysis was used to determine the composition of the gases above the electrolysis solution during and after each run.[7] Formate was analyzed for either by esterfication to methyl formate or by dehydration to CO, each followed by GC analysis. In a typical run, 9×10^{-5} mol of **2** in 75 mL of acetonitrile/water (1:2 v/v) was electrolyzed under CO_2 at ambient room temperature. After 1.1 h, 82 C had been passed, corresponding to 8 e^- per cobalt complex, and GC analysis revealed 1.8×10^{-4} mol of CO and 1.8×10^{-4} mol of H_2 as the only products, corresponding to a current efficiency of 94%.

The results for these electrolysis experiments, which were each performed at least six times, are shown in Table I. Compounds **1**, **2**, and **3** display current efficiencies of greater than 90% and rates of catalysis in terms of electrons passed per complex per hour ranging from 2 to 9 at ambient room temperature. Longer term electrolyses performed with complexes **1** and **2** underscore the catalytic nature of the observed reactions. For example, an electrolysis with 8.8×10^{-5} mol of complex **2** produced 5.1×10^{-3} mol of H_2 and 1.4×10^{-3} mol of CO after 19 h of electrolysis under a CO_2 atmosphere, corresponding to 164 turnovers or electrons passed per catalyst complex, and a current efficiency of 96%. Similar results were obtained from other runs with both **1** and **2**.

The nature of the catalytic reduction process was investigated further by several additional cpc experiments, the results of which are summarized as follows: (1) No carbon monoxide was detected when electrolyses were performed under a CO_2 atomosphere at potentials as negative as −1.6 V vs. SCE in the absence of the catalysts. (2) No carbon monoxide was detected when complexes

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(6) The gas-tight cell was a 250-mL three-necked 14/20 round-bottomed flask equipped with two side arms. The working electrode in all the experiments was mercury. The connection to the Hg was made through a Pt wire inserted through the bottom of the flask. The cell volume was 270 mL of which 185 mL was occupied by gases.

(7) Molecular hydrogen and carbon monoxide were determined on a 2 ft × $^1/_4$ in. column of molecular sieves 5A and a 12 ft × $^1/_4$ in. column of Poropak Q at 43 °C; carbon dioxide was determined on the Poropak column under the same conditions.

(8) Turnover numbers are calculated from the mol of electrons passed per mol of catalyst. Current efficiencies are calculated from the ratio of mol of product detected to the mol of product expected on the basis of a two-electron reduction of CO_2 and the measured number of C passed during the run.

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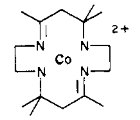
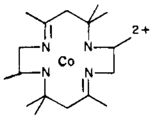
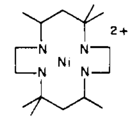
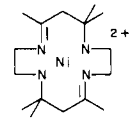
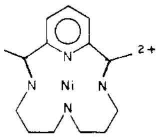
Table I

compd	electrode potential vs. SCE[a]	average current efficiency,[b] %	products, ratio[c]	turnovers per h at 23 °C[d]	solvent system
 1	−1.6	93	CO/H_2, 1:1	7.8	0.1 M KNO_3 in H_2O/CH_3CN 2:1 (v/v) or H_2O only
 2	−1.5	90	CO/H_2, 1:1	9	0.1 M KNO_3 in H_2O/CH_3CN 2:1 (v/v) or H_2O only
 3	−1.6	98	CO/H_2, 2:1	6	0.1 M $LiClO_4$ in H_2O/CH_3CN 2:1 (v/v)
 4	−1.5		*e*		
 5	−1.3	44	CO	2.1	0.1 M KNO_3 in H_2O/CH_3CN 2:1 (v/v)

[a] All cpc experiments were carried out at the cathodic $E^{1/2}$ or 0.1 V more negative than the $E_{p,c}^{1/2}$ for the $M^{2+/1+}$ couple in the solvent system used. [b] Averaged over numerous runs by using the following catalyst concentrations: compounds **1**, **2**, **3**, and **4** 1.2 mM; compound **5** 2.5 mM. [c] See footnote 5. [d] Turnovers per h per mol of catalyst for runs in which the catalyst concentration was 1.4–2.4 mM. A turnover is defined as 1 equiv of electrons passed through the electrolysis cell per mol of catalyst. Since the reduction products require two electrons for their formation, these numbers correspond to twice the mol of product formed per mol of complex per h. [e] Although catalysis has been observed with this compound in a number of solvent systems, reliable current efficiencies and rates have not been obtained.

1, **2**, or **4** were electrolyzed in dry Me_2SO in the presence of CO_2. However, when water was added to the closed cell containing one of the M^+ species generated under these conditions, both CO and H_2 were formed, and catalytic activity under electrolysis began. (3) No carbon monoxide was detected when complexes **2** or **3** were electrolyzed under Ar or N_2. When these complexes were electrolyzed in a CH_3CN/H_2O mixture under N_2, the only product formed was molecular hydrogen with current efficiencies as high as 80% for complex **2**. The rate of H_2 production in these electrolyses was approximately the same as the rate of CO + H_2 production when the complexes were electrolyzed under a carbon dioxide atmosphere. (4) No carbon dioxide was detected when either complex **1** or complex **2** was electrolyzed under an exclusively CO atmosphere, even after several hours, and no H_2 was produced in the absence of electrolysis under a CO atmosphere. Thus, the possibility of H_2 production via the water–gas shift reaction under these conditions was eliminated. An IR solution spectrum of complex **1** which had been electrolyzed under CO exhibited ν_{CO} at ca. 1900 cm^{-1} which was removed upon flushing the solution with Ar. (5) No carbon monoxide was detected after the direct interaction of H_2 with CO_2 in the absence or the presence of the complexes listed in Table I. (6) Trace amounts of formate were detected in catalytic runs with compounds **2** and **4**. However, formate was not stable under the conditions generated *during* the electrolyses. When formate was added to an electrolysis of complex **2** under N_2, a stoichiometric amount of CO_2 was produced based on mol of catalyst. (7) The rate of catalysis was increased significantly by an increase in temperature. For catalyst **1** (1.2 mM solution) electrolyzed at 40 °C, the rate of catalysis increased to 22 turnovers per h. (8) Cyclic voltammograms and IR spectra were taken of compounds **1**, **2**, **3**, and **4** isolated at the end of several runs. These were identical with CVs and IR spectra of the original compounds.

From these results, a number of conclusions can be drawn. First and foremost, an indirect electrochemical reduction of CO_2 has been accomplished at potentials between −1.3 and −1.6 V vs. SCE. The reduction is catalytic in metal complex, with activity not decreasing for periods as long as 24 h. In most cases, the catalyst was isolated at the end of the run in its original form. A protic source is also needed for the production of CO and H_2; in its absence, simple stoichiometric reduction of the complex is observed.

While detailed mechanistic information is still lacking, the fact that CO and H_2 are the major reduction products and that they occur only when a protic source is present suggests that both products may arise from a common intermediate which is most likely a metal hydride. Since the rate of H_2 production under N_2 is similar to the rate of CO + H_2 production under CO_2, it appears that CO_2 is competing effectively with protons for the reducing electrons in these systems. This is indeed encouraging since CO_2 has much poorer ligating abilities than does H^+. The intimate reduction of CO_2 may therefore proceed via direct attack of CO_2 on the proposed hydride species, obviating the necessity of its prior coordination at the metal center. Studies designed to confirm this hypothesis, and to improve the catalysis, are under way.

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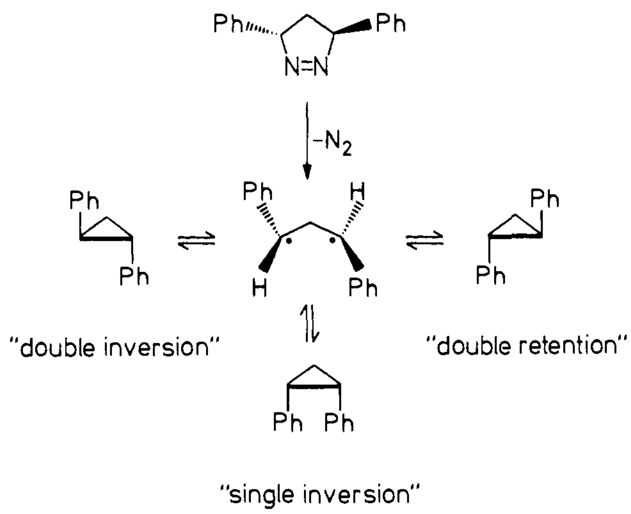
Transfer of Optical Activity in the Decomposition of (+)- and (−)-*trans*-3,5-Diphenyl-1-pyrazoline. Competing "Biradical" and "Cycloreversion" Pathways

Sir:

It is very tempting to suggest that stereomutations of cyclopropanes and the decomposition reactions of 1-pyrazolines both involve similar trimethylene intermediates (e.g., Scheme I). The stereochemical pattern of both reactions has been explained either by the implication of biradicals[1] (of varying nature[2]) or, in support of theoretical considerations,[3] via intermediate 0,0 trimethylenes (π-cyclopropanes).[4,5] Although major theoretical contributions[6] and elegant experiments[2,5,7] have greatly increased our knowledge of the involved intermediates, the outcome of new experiments seems rather unpredictable and dependent on the specific system. Studies with optically active 1-pyrazolines along this line are rather rare,[5] and we found a systematic investigation of a number of these systems rather attractive.

We report here, in the first experiments of a series, the photolysis and thermolysis of the title compounds (+)- and (−)-**1**. Both enantiomers, as well as the major reaction products (+)- and (−)-*trans*-1,2-diphenylcyclopropane (+)-**2t** and (−)-**2t**, were obtained optically pure from racemic material by direct chromatography on cross-linked triacetylcellulose[8] (Figure 1). In a typical run, saturated solutions of **1**[9] (1% in EtOH) or **2t**[10] (6% in EtOH) were injected on packed steel columns with EtOH as eluant; both the angle of rotation and the optical density were recorded continuously.[11] Due to base line separations and the use of preparative columns the pure enantiomers could be easily isolated. Their optical purities were controlled by analytical runs and their chiroptical data, rotations [(−)-**1**: $[\alpha]^{22}_{\mathrm{D}}$ −817°, $[\alpha]^{22}_{365}$ −6680° (*c* 0.023 EtOH); (−)-**2t**: $[\alpha]^{22}_{\mathrm{D}}$ −423°, $[\alpha]^{22}_{365}$ −1987° (*c* 0.0087 EtOH)] and molar ellipticities [(−)-**1**: $[\theta]_{332}$ −44 090° (EtOH, 1.3×10^{-3} M); (−)-**2t**: $[\theta]_{230}$ −114 021° (EtOH, 4.5×10^{-4} M)].[12]

Scheme I



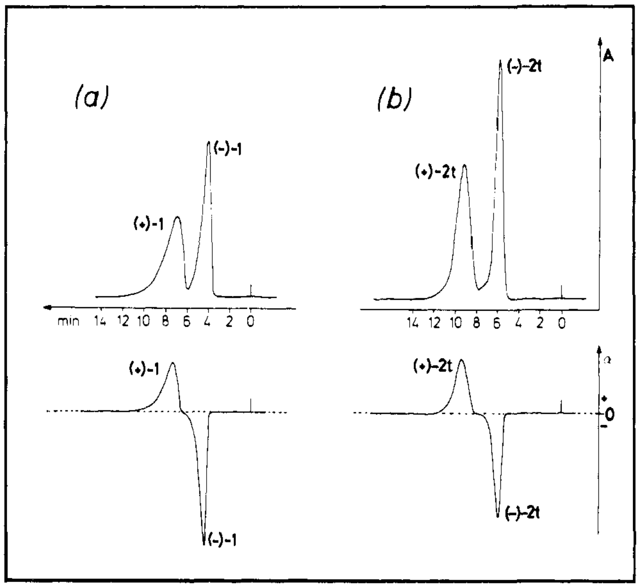


Figure 1. High-performance LC chromatograms for the separation of (a) (±)-**1**, (b) (±)-**2t** on cross-linked triacetylcellulose;[8,11] (α) angle of rotation at full lamp (Hg) intensity with filters removed; (A) absorbances at 330 nm [(±)-**1**] and 254 nm [(±)-**2t**].

Their absolute configurations were either known [(+)-/(−)-**2t**][13] or established [(+)-/(−)-**1**] by comparison of ORD and CD spectra with those of known compounds,[5a,b,14] as well as by application of an octant rule.[15]

Degassed 1.2×10^{-3} M solutions of (+)-**1**[16] in a variety of solvents were irradiated with monochromatic (330 ± 10 nm) ultraviolet light (lamp: XBO 1600 from Osram, monochromator: High Intensity Monochromator 33-86-79 from Bausch & Lomb) or thermolyzed in a constant temperature (75 ± 0.1 °C) bath until completion. Reactions were followed both by UV and CD. In a typical experiment (Figure 2) the CD maximum of (+)-**1** at 332 nm (corresponding to the n → π^* transition in **1**) decays gradually during the reaction under the formation of (−)-**2t** with

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(4) In order to accommodate the experimental data the following mechanistic proposals with their stereochemical consequences have been suggested previously:[2] (a) stereorandom trimethylene biradicals; (b) single methylene rotation; (c) double methylene rotation via 0,0 trimethylenes (π-cyclopropanes).

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(11) Columns 8 mm × 250 mm; particle size 30–50 μm (7 μm has recently become available and is now being tested); flow rates 1.9 mL/min for **1**, 1.2 mL/min for **2t**; polarimeter flow cell from Hellma GmbH + Co, D-7840 Müllheim, Germany, length 100 mm, volume 57 μL; Perkin-Elmer 241 polarimeter; eluant 96% EtOH.

(12) Rotations and molar ellipticities have been determined for all enantiomers in a variety of solvents; for brevity only a few values are listed. The data compare well with the literature values for (+)-**2t**[13a] and (−)-**2t**;[13b] (+)- and (−)-**1** have been obtained here for the first time.

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(16) Experiments with both (+)- and (−)-**1** have been carried out; for clarity only one is used.

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