Reduction of Co-ordinated Carbon Dioxide to Carbon Monoxide *via* Protonation by Thiols and other Brønsted Acids promoted by Ni-Systems: a Contribution to the Understanding of the Mode of Action of the Enzyme Carbon Monoxide Dehydrogenase

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Carbon dioxide co-ordinated to Ni^0 is easily reduced to bound carbon monoxide by R–SH (R = H, alkyl, benzyl, phenyl, and substituted phenyl) and other Brønsted acids, providing a reasonable model for the Ni-containing enzyme carbon monoxide dehydrogenase.

In the last few decades the utilization of carbon dioxide in synthetic chemistry has been of wide interest as this molecule is abundant, non-hazardous, and cheap.[1,2] A great effort is currently being made to isolate and characterize the enzymes involved in the 'natural' reduction of CO_2 by plants (both C_3 and C_4) and bacteria, as the knowledge of their mode of action may be invaluable for genetic engineering, modelling photosynthesis, and mimicking the natural carboxylation in synthetic chemistry. In particular, the carbon monoxide dehydrogenase (CODH) enzyme is responsible for the reduction of carbon dioxide to carbon monoxide [equation (1)] in anaerobic chemotrophic bacteria.[3] It is known to be a tetramer, $\alpha_2\ \beta_2$, and to contain 2 Ni, 1 Zn, 9—11 Fe, and 12—14 free acid active sulphurs.[4] It has been proposed that the active site of the enzyme for carbon dioxide reduction is the Ni atom[5,6] that in the inactive enzyme (e.s.r. silent) is in the Ni^{II} state and in the operating enzyme (e.s.r. active) may be in the Ni^{I} state.[5a] Both the interpretation of the CO_2

reduction mechanism and of the role of –SH, Fe, and Zn present some controversial points which will require more work.

$$\mathrm{CO_2 + 2\,H^+ + 2\,e^- \rightarrow CO(bound) + H_2O} \tag{1}$$

We have discovered that the complex $\mathrm{Ni(PCy_3)_2(CO_2)}$ (**1**)[7] (Cy = cyclohexyl) dissolved in toluene under dinitrogen reacts easily with RSH (R = H, alkyl, phenyl, or substituted phenyl) to afford Ni-bound-CO. This represents the first clear evidence of the protonation of a carbon dioxide molecule co-ordinated to a metal centre and of its reduction to carbon monoxide and is relevant to the mode of action of CODH. Compound (**1**) in toluene under dinitrogen is in equilibrium with (**2**) [equation (2)]. The i.r. spectrum of the solution shows bands due to the free and to the co-ordinated carbon dioxide at 2335 and 1745 $\mathrm{cm^{-1}}$ respectively, the intensity of the band at 2335 $\mathrm{cm^{-1}}$ increasing with time. When dry, gaseous $\mathrm{H_2S}$ is added to this solution the i.r. band of the co-ordinated carbon dioxide disappears and two bands appear at 1980 and 1912 $\mathrm{cm^{-1}}$, due to the bound-carbonyl groups. These bands are in fact due to the $\mathrm{Ni(PCy_3)_2(CO)_2}$ (**3**) species,[7,8] isolated from the reaction mixture together with a second Ni species, containing sulphur and phosphorus, analysing for $\mathrm{(PCy_3)_2Ni(SH)_2}$, and showing a weak i.r. band at 2560 $\mathrm{cm^{-1}}$ assigned to ν(S–H). The i.r. and ^{1}H n.m.r. spectra of the solution showed that water was also formed in the reaction. The neat reaction involving $\mathrm{CO_2}$ is represented by equation (1) and $\mathrm{Ni^0}$ is the electron source.

$$\underset{(\mathbf{1})}{\mathrm{Ni(PCy_3)_2(CO_2)}} \underset{\mathrm{CO_2}}{\overset{\mathrm{N_2}}{\rightleftarrows}} \underset{(\mathbf{2})}{\mathrm{Ni(PCy_3)_2N_2}} \tag{2}$$

When PhSH was used, (**3**) and $\mathrm{(PCy_3)_2Ni(SPh)_2}$ (**4**) were isolated from the solution. If these species were left in solution for a long time carbonyl conversion took place and a new species [ν(CO) at 1970 $\mathrm{cm^{-1}}$], still under investigation, was formed.

When the reaction was carried out under nitrogen, the yield of the dicarbonyl (0—10% based on Ni) was strongly dependent on the concentration of the Ni–$\mathrm{CO_2}$ complex in solution and decreased with the time elapsed between the dissolution of (**1**) in toluene and the addition of the Brønsted acid. Conversely, when the reaction was carried out under carbon dioxide [that displaces equilibrium (2) to the left] stoicheiometric yields of (**3**) were obtained [equation (3)]. This clearly demonstrates that carbon dioxide must be co-ordinated to $\mathrm{Ni^0}$ in order to be converted into carbon monoxide. The protonation–reduction reaction with PhSH was fast and 0.3 mmol of bound $\mathrm{CO_2}$ were converted in *ca.* one minute as demonstrated by spectroscopic measurements. The disulphide PhS–SPh is formed, but does not accumulate and cannot be isolated at the end of the reaction, as it adds to $\mathrm{Ni^0}$. Indeed, in a separate reaction we have found that an authentic sample of PhSSPh, under controlled conditions, reacts with $\mathrm{[(PCy_3)_2Ni]_2N_2}$[9] to afford $\mathrm{(PCy_3)_2Ni(SPh)_2}$, equation (4)]. These phosphine–sulphido-complexes are not stable in solution for long, especially in the presence of an excess of free sulphide or disulphide, as elimination of the phosphorus ligand takes place and the polymeric insoluble material $\mathrm{[Ni(SPh)_2]}_n$ is obtained.

$$\mathrm{3\,(P)_2Ni(CO_2) + 4\,PhSH \rightarrow (P)_2Ni(CO)_2 + 2\,(P)_2Ni(SPh)_2 + CO_2 + 2\,H_2O} \tag{3}$$

$$\mathrm{(P) = PCy_3}$$

$$\mathrm{[(PCy_3)_2Ni]_2N_2 + 2\,PhS{-}SPh \rightarrow 2\,(PCy_3)_2Ni(SPh)_2 + N_2} \tag{4}$$

N.m.r. techniques (^{1}H, ^{13}C, and ^{31}P) are not useful for a kinetic study of the $\mathrm{CO_2}$ reduction as this is too fast on the n.m.r. time scale, at least under the 'quasi-physiological' conditions we have studied to date.† Dry HCl has been used as a proton donor and the same reduction reaction takes place, but at a lower rate, together with the possible addition of HCl to (**2**) to afford the hydrido species $\mathrm{(P)_2NiHCl}$.[9] That the Ni-promoted $\mathrm{CO_2}$ reduction to CO in our case requires 'protons plus electrons' and not 'hydrogen' is demonstrated by the fact that (**1**) and dihydrogen under the same reaction conditions (and in the same solvent) used for the protonation reaction do not afford the dicarbonyl (**3**). Organic products and a $\mathrm{Ni^{II}}$ hydroxo species were formed in this reaction, which was much slower than the protonation and very sensitive to moisture. When the hydrogenation was monitored by n.m.r. techniques (^{1}H, ^{13}C, ^{31}P) a broadening of the ligand peaks indicated that a $\mathrm{Ni^I}$ paramagnetic species was formed, but disappeared during the reaction. The proton requirement for $\mathrm{CO_2}$ reduction by our systems is demonstrated by the fact that PhSNa is not active in strictly anhydrous media and is in agreement with the finding that the optimum carbon dioxide reduction by CODH seems to require an acidic pH.[6]

$$\mathrm{2\,CO_2 + 2\,e^- \rightarrow CO + CO_3^{2-}} \tag{5}$$

$$\mathrm{2\,PhSH \rightarrow 2\,PhSH^{+\bullet} + 2\,e^- \rightarrow 2\,PhS^{\bullet} + 2\,H^+ + 2\,e^- \rightarrow PhSSPh + 2\,H^+ + 2\,e^-} \tag{6}$$

However, the fact that PhSH is the best 'protonating and reducing' agent can be explained by noting equation (6), which poses a question on the possible role of the –SH groups in the $\mathrm{CO_2}$ to CO reduction by CODH enzyme, and on the role of the disulphide reductase enzyme whose presence seems to be necessary for CODH activity. We have also used $\mathrm{NiL_2X_2}$(L = monodentate phosphine; $\mathrm{L_2}$ = bidentate or polydentate phosphorus or nitrogen ligands; X = Cl, Br, or I)[10] and $\mathrm{NiL_2X}$ complexes (L = $\mathrm{PCy_3}$;[9] $\mathrm{L_2}$ = $\mathrm{Cy_2PCH_2CH_2PCy_2}$, X = Cl or Br) in the carbon dioxide reduction by thiols and other Brønsted acids. In the dark all $\mathrm{Ni^{II}}$ complexes were inactive, and this agrees with the results found *in vivo*. Conversely, $\mathrm{Ni^I}$ complexes interact with carbon dioxide in the absence of thiols, and although the co-ordination of $\mathrm{CO_2}$ to the metal centre could not be clearly demonstrated, carbonyl and carbonates were formed according to equation (5).[10] The addition of PhSH to $\mathrm{(PCy_3)_2NiCl}$ under $\mathrm{CO_2}$ produces small amounts of the dicarbonyl complex (**3**).

$\mathrm{Ni^0}$, thus, is by far the most active catalyst in carbon dioxide reduction and selectively affords CO, as demonstrated by gas chromatographic analyses that confirm the absence of formates and oxalates. The highly selective $\mathrm{CO_2}$ to CO reduction achieved with $\mathrm{Ni^0}$ and Brønsted acids must be interpreted in terms of a preliminary co-ordination of carbon dioxide to $\mathrm{Ni^0}$

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† All the reactions were carried out at room temperature and the n.m.r. spectra were run at 27 °C trying to repeat conditions close to the 'physiological' ones. In these conditions only the spectra of the starting complex and of the final product were observed with ^{1}H, ^{13}C, and ^{31}P spectroscopy. *Selected spectroscopic data*: the ^{31}P n.m.r. spectrum of (**1**) in toluene has a slightly broadened singlet centred at 36.15 p.p.m., with respect to 85% $\mathrm{H_3PO_4}$. The $^{13}\mathrm{CO_2}$ spectrum was used to evaluate $J_{\mathrm{P-C}}$ = 14.8 Hz.[7,10] The use of $^{13}\mathrm{CO_2}$ (25% enriched) did not help to get a better resolution for the ^{31}P signal and the multiplicity was not clear. Addition of PhSH to the n.m.r. tube changed the spectra. Two singlets were observed in the ^{31}P spectrum at 39.51 and 8.31 p.p.m., assigned to (**3**) and (**4**) respectively, while the ^{13}C spectrum showed a singlet at 202.98 p.p.m. due to (**3**) (carbonyl groups) in addition to the signals of the ligands. Intermediate species were not detected under these conditions.

with electron transfer from the metal to the cumulene that results in a CO_2^--like state and a proton-plus-electron transfer to the co-ordinated CO_2, that converts into the carbonyl species, most probably through the formation of the hydroxocarbonyl $L_nNi(CO_2H)$. The protonation of carbon dioxide as an essential step for its reduction to CO has also been proposed in the photoreduction catalysed by Ru systems.[11,12] Our results might also help to interpret the role of iron–thiolato complexes[13] used as catalysts in the electroreduction of CO_2. The high selectivity shown by our systems matches the finding that $Ni(cyclam)^{2+}$ is a good electrocatalyst[14] for the selective reduction of CO_2 to CO. We are currently using more sophisticated techniques under 'non-physiological' conditions (low temperature, high pressure) for detecting the intermediate species.

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