

Photochemical, Metal-promoted Reduction of Carbon Dioxide and Formaldehyde in Aqueous Solution

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The photochemical reduction of carbon dioxide in aqueous solution containing transition metal salts has been investigated. The reduction to formic acid and formaldehyde as observed in earlier studies was confirmed. By irradiating solutions of formaldehyde and methanol, reduction to methanol and methane, respectively, could also be observed.

Photochemical conversion of carbon dioxide into fuels is an attractive procedure for long term storage of solar energy. In principle this process is already used in nature in the conversion of carbon dioxide into carbohydrates by the green plants. This type of conversion has also been done in the laboratory, but much of the early work is evidently difficult to reproduce.¹ More recent work, however, has clearly established that carbon dioxide may be reduced to formic acid and formaldehyde by ionizing radiation² and UV-light³ in the presence of iron(II). It has also been shown that formic acid and methanol may be formed fairly efficiently on electrolytic reduction of carbon dioxide.⁵

Very recent communications have also reported that small amounts of methane may be produced by UV-irradiation of a mixture of carbon dioxide and water, adsorbed on a single crystal face of strontium – titanium(IV)oxide,^{4a} and that photoinduced electrolytic reduction to methanol is quite facile.^{4b}

We have now studied if the iron(II) system used earlier³ for the reduction of carbon dioxide to formaldehyde can also be used to produce methanol and methane. We have furthermore studied some other metal catalysts, cobalt(II), chromium(II) and ruthenium(II), and the effect of added organic ligands like 2,2'-bipyridyl and phenanthroline. Some preliminary results have been reported earlier.^{4c} Due to the low "steady state" concentration of

formaldehyde, analytical problems prohibit the GLC detection of methanol and methane from the direct reduction of carbon dioxide. When more concentrated solutions of formaldehyde are used, however, methanol formation can be observed, and by photolysis of methanol solutions even methane formation could be confirmed.

In the reduction experiments, an aqueous solution of the desired metal salt was saturated with carbon dioxide and irradiated under continuous bubbling of carbon dioxide through the solution. UV-light of 254 nm was generally used, but in some experiments visible light was employed.

The reduction in the presence of iron(II) rapidly yielded a low, stationary concentration of formic acid and formaldehyde (Table 1). Similar results were obtained with cobalt(II) and chromium(II). In the absence of metal ions no reduction occurred.

Since the oxidized form, iron(III), should be capable of reoxidizing the reduced products, attempts were made to increase the yield of reduction products, in particular formaldehyde and methanol, by chemical reduction of iron(III) during the irradiation. Neither of the reducing agents, metallic iron and zinc amalgam, was capable of increasing the yield of formaldehyde and reduction products like methanol could not be detected. This was also the result of continuous electrolytic reduction of iron(III) to iron(II) at a reduction potential sufficiently low not to reduce carbon dioxide electrolytically. Furthermore, addition of fluoride to scavenge iron(III) led to a sharp decrease in the yield of reduction products. Contrary to intuition, the accumulation of iron(III) is thus not the major factor that is responsible for the low yields of formic acid and formaldehyde.

Nor are the relative absorption properties of the

Table 1. Irradiation of CO₂ in Fe²⁺-solution.

Exp. No.	Me ²⁺	mmol	Lamp	Irradiation time/min	Formed HCHO	Yield based on Me ²⁺ reacted/%
1	Fe ²⁺	3.5	Hanovia UV	95	$\cong 2 \times 10^{-3}$	$\cong 5.7 \times 10^{-2}$
2	Fe ²⁺	3.5	Hanovia UV	257	$\cong 2 \times 10^{-3}$	$\cong 5.7 \times 10^{-2}$
3	Fe(bipy) ₃ ²⁺	0.35	Hanovia UV	120	$\cong 2 \times 10^{-3}$	$\cong 5.7 \times 10^{-1}$
4	Fe ²⁺ + Zn(Hg)	3.5	Hanovia UV	30	$< 2 \times 10^{-3}$	$< 5.7 \times 10^{-1}$
5	Fe ²⁺ + Fe	3.5	Hanovia UV	150	$< 2 \times 10^{-3}$	$< 5.7 \times 10^{-1}$
6	Fe ²⁺	1	Black box UV	720	$\cong 7 \times 10^{-4}$	$\cong 7 \times 10^{-2}$

continous reduction of Fe³⁺

Table 2. Irradiation of HCHO in Me²⁺-solution in a Rayonet photoreactor at 253.7 nm.

Exp. No.	Me ²⁺	mmol	Time/h	MeOH formed/mmol	Yield based on reacted Me ²⁺ /%
1	Cr ²⁺	4.0	19	0.226	5.7
			23	0.323	8.1
2	Fe ²⁺	4.0	21	0.326	8.2
			24	0.324	8.1

Table 3. Irradiation of MeOH in Cr²⁺-solution in a Rayonet photoreactor at 2537 Å.

Me ²⁺	mmol	Time/min	MeOH/mmol at start	CH ₄ /mmol formed	Yield based on reacted Me ²⁺ /%
Cr ²⁺	1.0	75	49.4	1.8×10^{-5}	3.6×10^{-5}

oxidized and the reduced form of the metal ions the only factor. Iron(III) absorbs about 10³ times more strongly than iron(II) in the UV region. Even at a moderate concentration, iron(III) will therefore absorb most of the incident light and inhibit further reduction. Addition of 2,2'-bipyridyl, which results in the formation of the trisbipyridine complexes of iron(III) and (II), which have about the same absorption coefficient in the UV, resulted in an increase in the yield of the reduced products. This increase did not correspond to the large increase in the relative absorption of the iron(II) species, however, (Table 1). Since the bipyridine-iron(II) complex absorbs strongly in the visible region, irradiation with visible light was carried out. However, neither tris-2,2'-bipyridyl iron(II) nor the corresponding ruthenium(II) complex did promote reduction of carbon dioxide with visible light.

A major part of the present work has been devoted to studying the further reduction of form-

aldehyde. Since neither methanol, nor methane could be detected in the reduction of carbon dioxide, more concentrated solutions of formaldehyde were studied (Table 2). Again the major reduction product, in this case methanol, reached a low, stationary level, which was sufficiently low to cause serious analytical problems. The values reported in Table 2 are fairly reproducible, however. One explanation for the low efficiency of the reduction of formaldehyde is the extensive hydration in aqueous solution (*cf.* Ref. 6). Since electrolytic reduction of both carbon dioxide and formaldehyde to methanol is fairly efficient, this can not be the only explanation.

Finally, photoreduction of methanol was studied. This reduction is very sluggish and only very low yields of methane were obtained (Table 3).

An extensive discussion of the mechanistic aspect of the reduction of carbon dioxide is not possible at this point. In principle, metal hydrides could

Table 4. Rate constants for some of the electron transfer processes involved in reduction of carbon dioxide to methane by solvated electrons (Ref. 7).

Eqn.	Rate, $M^{-1} S^{-1}$
(2)	7.7×10^9
(4)	1.4×10^8
(6)	$< 10^7$
(8)	$< 10^4$
(10)	$10^8 - 10^{10}$
(11)	2.3×10^{10}
(12)	1.1×10^6
(14)	$< 10^6$

also form from hydrogen atoms and metal ions, *e.g.* eqn. 13, but it does seem somewhat unlikely that chromium and iron hydrides should be equally efficient as reducing agents (Table 2).

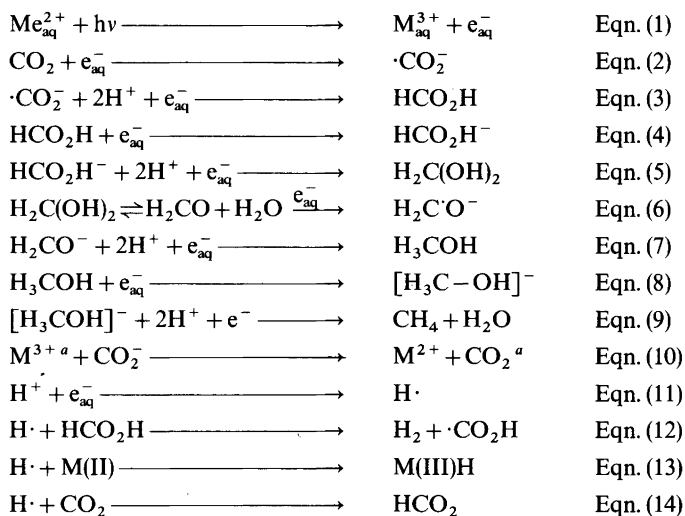
It is interesting to note, that the relative efficiencies of the reduction steps parallel the abilities of the intermediates to capture solvated electrons (Table 4) (for extensive discussions of the reactions of solvated electrons, see Ref. 7). It therefore seems more likely that reduction proceeds *via* solvated electrons, generated photochemically according to eqn. 1.

Relative to carbon dioxide and formic acid, formaldehyde and in particular methanol, are very poor electron acceptors in water solution (Scheme 1,

Table 4). It is further evident that the rate of hydrogen abstraction from the reduced products by hydrogen atoms, (*e.g.* eqn. 12), which leads to reoxidation, is several powers of ten slower than electron capture by carbon dioxide and formic acid.⁷ This reaction is thus unlikely to be responsible for the low, stationary concentrations of formic acid and formaldehyde. A more likely candidate is the reaction (10), Scheme 1, which is the formal reversal of the combined reactions (1) and (2). For cobalt, this reaction has been investigated and it may be extremely rapid (Table 4).⁸ It may in fact be so rapid that even if the concentration of the oxidized metal species, *e.g.* iron(III) is decreased by several powers of ten by chemical or electrolytic reduction, the overall rate of reaction (10) is essentially unaffected. This may explain the present results, but further studies are required to ascertain the mechanism of the reduction. Also, in order to improve the yield of methanol, a more sophisticated reducing system is required. Nevertheless, it is encouraging that direct reduction to methanol is possible in practice.

EXPERIMENTAL

Irradiation of CO_2 in Fe^{2+} -solution. The reaction was performed in a photoreactor with a Hanovia immersion lamp No. 6515-34, 450 W.



Scheme 1. ^a M = Co, Ref. 8.

All reagents were of analytical grade. A 0.01 M solution of iron(II) was made by dissolving 2.78 g of heptaaquairon(II) sulfate in 1 l of 0.001 M sulfuric acid. From this solution, 350 ml were transferred to the reaction vessel and deaerated with a stream of carbon dioxide for 2 h. A sample of 3 ml was withdrawn with a syringe and used as reference. While carbon dioxide was continuously bubbled through the solution it was irradiated. Samples were taken at suitable intervals and analyzed for formic acid, formaldehyde and methanol. Some representative results are presented in Table 1.

Formic acid was analyzed as its benzyl ester⁹ on a Pye 104 gas chromatograph with a flame ionization detector using a 2 m × 6 mm glass column packed with PEG 20 m 20% on Chromosorb W at 117.5 °C and with propionic acid as internal standard.

Formaldehyde was analyzed spectrophotometrically by the chromotropic acid method.¹⁰

Analysis for methanol was performed on a Varian 1400 chromatograph with a FID equipped with a 2 m × 3 mm stainless steel column packed with Carbowax 20% on Chromosorb W at 70 °C.

Irradiation of formaldehyde in Me²⁺-solution. Formaldehyde was prepared by hydrolysis of recrystallized and sublimed trioxane in the following way: 3.003 g trioxane (0.033 mol) in 20 ml 0.25 N sulfuric acid was kept at about 95 °C for 24 h. The cooled mixture was titrated to pH 3 with 1 M sodium hydroxide. 20 ml of this solution was transferred to a quartz tube. Dry and oxygen free nitrogen was introduced at the bottom by a polyethylene tubing via a rubber septum equipped with a narrow syringe needle. Deaeration was effected by purging the solution with nitrogen for about 2 h.

A 0.2 M chromium(II) solution was prepared by passing 1.06 g hexaaquachromium(II) chloride in 20 ml of 0.001 N sulfuric acid through a Jones' reductor. Twenty ml of the bright blue solution of chromium(II) was combined with the formaldehyde solution in the reactor to give an approximately 0.1 M chromium(II) solution.

An 0.2 M iron(II) solution was prepared by dissolving 2.78 g septaaquairon(II) sulfate in 50 ml of 0.001 N sulfuric acid under nitrogen atmosphere. Twenty ml of this solution was transferred to the reaction tube with a syringe.

After addition of Me²⁺ to the formaldehyde solution a sample was removed for UV-spectroscopy and GLC analysis. This sample was then kept in the dark under nitrogen to serve as reference during the experiment.

The irradiation was performed in a Rayonet photochemical reactor fitted with a total of 16 RPR 253.7 nm lamps. The reaction mixture was stirred by purging with nitrogen during the irradiation. Quantitative analysis of methanol was performed

partly on a Pye Unicam GCV and partly on a Varian 200 gas chromatograph with FID detectors on 2 m × 3 mm glass column packed with Porapak T 80–100 mesh at 110 and 125 °C, respectively, and with ethanol as internal standard.

Irradiation of methanol of Cr²⁺-solution. Ten ml of 20% methanol of analytical grade was transferred into a quartz tube. Deaeration of the solution was then effected by purging for 2 h with dry and oxygen free nitrogen, which was introduced at the bottom of the tube by a polyethylene tubing.

A 0.2 M solution of chromium(II) (10 ml) was then added. A reference sample was removed and the remaining solution was irradiated at 253.7 nm in a Rayonet photoreactor. The volatile products were collected in a gas burette and analyzed at 120 °C on a Varian 1400 gas chromatograph equipped with a 2 m × 3 mm stainless steel column packed with Porapak T.

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