Photoinduced Transformation of Carbon Monoxide in Aqueous Solution

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The photoinduced conversion of CO in aqueous solution under the influence of vacuum-uv radiation at $\lambda = 185$ nm has been investigated at pH values ranging from 2 to 13. Formaldehyde, glyoxal, carboxylic acids and small amounts of glycol were determined as final products. Initial quantum yields for product formation have been determined. A probable reaction mechanism is presented.

Introduction

It has been shown previously that the action of gamma-radiation on aqueous carbon monoxide leads to the formation of formic acid, formaldehyde and glycol [1]. If suitable organic acceptors are present, incorporation of CO as a carbonyl group can be achieved in aqueous solutions [2–5] as well as in n-alkanes [6]. Thereby CHO radical and its hydrated counterpart, $\dot{\text{C}}\text{H}(\text{OH})_2$, have been postulated as intermediates in the reduction and carbonylation processes. The existence of the CHO radicals has been proved by ESR spectroscopy [7]. On the other hand, the reaction of CO with OH resulting in COOH or HCOO radicals has been demonstrated by pulse radiolysis [8]. Further investigations have shown that incorporation of CO in aqueous methanol using vacuum-uv radiation at 185 nm [9] or 123.6 nm [10] is also possible.

The present work was undertaken in order to investigate the possibility of the photoinduced conversion of aqueous carbon monoxide in the absence of organic acceptors. Quantum yields for product formation have been measured at pH values ranging from 2 to 13, and a probable reaction mechanism is presented to explain the results.

Experimental

High purity CO (Messer-Griesheim, Austria), p.a. grade chemicals (Merck) and four times distilled water were used for preparation of the solutions. Irradiation of aqueous carbon monoxide (1×10^{-3} mol dm $^{-3}$ CO) was performed at $20 \pm 1^\circ\text{C}$ in a temperature-controlled vessel with 4π -geometry [11,12]. The 185 nm line of a low-pressure Hg lamp (Hanau TNN 15/32) was used for the photolysis of water. For adjustment of the pH, p.a. HClO $_4$ or p.a. NaOH were applied. All solutes used were transparent for the simultaneously emitted uv-light at 254 nm. Actinometry for the 185 nm line was carried out using 5 mol dm $^{-3}$ ethanol with $Q(\text{H}_2) = 0.40$ [13]. The integral photon flux at 185 nm was found to be $I_0 = 8 \times 10^{16}$ quanta ml $^{-1}$ min $^{-1}$.

Formaldehyde was determined by spectrophotometry using the method of Hantzsch [14], whereby the reagent yields diacetyldihydrolutidine, whose absorption is monitored at 412 m ($\epsilon = 8000$ dm 3 mol $^{-1}$ cm $^{-1}$). The presence of glyoxal does not interfere the measurement. Glyoxal was also determined spectrophotometrically, by means of 2,4-dinitrophenylhydrazine as the reagent ($\lambda = 575$ nm, $\epsilon = 2160$ dm 3 mol $^{-1}$ cm $^{-1}$) [5,15]. The total yield of carboxylic acids formed was measured by differential titration with NaOH at pH-values below 7 and with HCl at higher pH-values. The identification of the formic, oxalic and glyoxalic acids was performed by paper chromatography [16].

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Results and Discussion

The action of vacuum-uv-light on water results in its photolysis into H and OH radicals [11, 12, 17] and to a smaller extent in formation of hydrated electrons, e_{aq}^- [11, 12]:

The quantum yields (Q) at 185 nm are: $Q(H) = Q(OH) = 0.33$ and $Q(e_{aq}^-) \leq 0.03$ [11]. In acid solution, e_{aq}^- are converted into H atoms, whereas in alkaline medium the opposite process takes place:

The primary products of water photolysis (OH, H, and e_{aq}^-) are subsequently reacting with CO to produce secondary radicals and final photoproducts. As will be discussed below, the main products to be expected are formaldehyde, glyoxal and carboxylic acids.

The dependence of the formaldehyde yield in aqueous solutions saturated with CO ($10^{-3} \text{ mol dm}^{-3}$) on the absorbed vuv-dose at pH 2 and 7 is shown in Figure 1. The initial quantum yield (Q_i) is considerably higher at pH 2 than at pH 7. The saturation like behaviour at higher doses indicates the occurrence of back reactions.

The yield-dose curves for glyoxal formed under the same experimental conditions are presented in Figure 2.

The total yield of carboxylic acids (formic, oxalic and glyoxalic acid) as determined at pH 7 and 12 is presented in Fig. 3 as a function of vuv-dose. The acids yield at pH = 12 is markedly higher as compared to the neutral one.

The yields of the final products (formaldehyde, glyoxal and carboxylic acids) are presented in Fig. 4 as a function of pH. The initial quantum yields (Q_i) of the same products are given in the Table inserted in Figure 4. The most conspicuous feature is the increase of the carboxylic acids yield at pH > 10; their total quantum yield is exceeding unity at pH 13.

Fig. 1. Formation of formaldehyde at pH = 2 (A) and 7 (B) by reduction of CO in aqueous solution as a function of u.v.-dose at $20 \pm 1^\circ \text{C}$.

Fig. 2. Formation of glyoxal at pH = 2 (A) and 7 (B) by reduction of CO in aqueous solution as a function of u.v.-dose at $20 \pm 1^\circ \text{C}$.

Fig. 3. Total yield of carboxylic acids produced from CO in aqueous solution at $20 \pm 1^\circ \text{C}$ as a function of u.v.-dose at pH = 7 (A) and 12 (B).

Fig. 4. pH-dependence of the photoinduced formation of aldehyde (A), glyoxal (B) and carboxylic acids (C) in aqueous solution at $20 \pm 1^\circ\text{C}$. Applied u.v.-dose: $I = 2.4 \times 10^{17}$ hv. ml of $\lambda = 184.9$ nm. Insert: Initial quantum yields (Q_1) of the products.

A) Acid and Neutral Solutions

The following reactions are expected to take place in acid and neutral media:

Hence, in weak acid solutions ($\text{pH} \geq 4.8$) only oxalate is formed:

In addition to the formic and oxalic acids, glyoxalic acid is also produced by combination of HCO and

COOH (or CO_2^-) transients, e.g.:

Further, combination of the present free radicals is also very likely, e.g.

At higher doses, primary and secondary radicals will attack the final products with increasing probability. These reactions will in part lead to products different from those mentioned before, e.g.

In analogy to HCHO (reactions (17) and (18)) also glyoxal and carboxylic acids can be decomposed by attack of H, OH and other intermediated occurring during the irradiation. Small amounts of glycol were actually detected among the products. Reactions of this type will contribute to the saturation-like behaviour observed in Figures 1–3.

The formation of hydrogen gas was detected by gaschromatography, but its yield was not determined at present.

Figure 4 shows that the major part of photo-products is present as carboxylic acids at all pH's. This may be explained, at least in part, by assuming that the HCO radicals are available in hydrated form [5, 26, 27]:

In a related study on photoinduced degradation of formaldehyde [28] it has been shown that the hydrated formyl radicals, HC(OH)_2 , tend to disproportionate to formic acid and hydrated formaldehyde,

whereas hydrated glyoxal does not arise:

Finally, reaction (6) being somewhat slower than reaction (8), secondary H atom reactions will be more efficient than OH reactions in competing with attack on CO.

In neutral and acid solutions, the total yield of final products is smaller than the yield for water splitting [11]. This may reflect a competition between in-cage recombination of H and OH and reaction with CO. Enhanced formaldehyde and glyoxal yields in acid medium probably reflect reaction (4); in neutral solution, attack of e_{aq}^- on CO should give rise to carboxylic acids, as discussed below.

B) Alkaline Solutions

The total yield of formic, oxalic and glyoxalic acid formed by the photoinduced conversion of CO in basic solution (pH = 12) as a function of the vuv-dose is presented as curve (B) in Figure 3. In this case the total yield of carboxylic acids is much higher compared to that one observed at pH = 7.

In addition to water photolysis, absorption of 185 nm light by OH_{aq}^- ions ($\epsilon = 3600 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ [29]) must be taken into account in alkaline solutions. However, this process will essentially lead to the same primary photoproducts as water photolysis by virtue of

and the fact that reaction (5) will tend to convert primary H atoms from water photolysis into e_{aq}^- .

Further to be taken into account is the dissociation of OH radicals:

As mentioned before (Fig. 3 and 4) the total yield of carboxylic acids increases strongly with increasing pH. The glyoxal yield decreases correspondingly, whereas the formaldehyde yield remains constant. A comparable increase in alkaline medium was found for the formation of formic acid in the γ -radiolysis of

aqueous CO [1]. The magnitude of the yields indicates that a chain reaction must be involved.

As mentioned above (reaction 5), the H-atoms are converted into e_{aq}^- in alkaline solutions. Reaction (23) is also responsible for the increase of e_{aq}^- yield, hence

The $\dot{\text{C}}\text{O}_{\text{aq}}^-$ transients are identical with HCOOH^- species, which can initiate a chain reaction with OH_{aq}^- [1, 5], namely

The $\dot{\text{C}}\text{OO}^-$ species lead to the formation of oxalate (reaction 11) and glyoxalic acid

Nothing is known about the reaction behaviour of CO_{aq}^- , although their participation in the chain process was suggested previously [1]. A clue can be seen in the decrease in glyoxal formation at high pH values (Fig. 4), which shows that reaction (7b) is inefficient under these conditions. Reaction (7a) seems to take place since formaldehyde is found up to pH 13, but it might be assumed that its rate constant is much smaller than in neutral solution.

Depending on the pH of the solution the following equilibrium is conceivable:

This postulation could contribute to a better understanding of the obtained product yields.

Conclusion

It has been shown for the first time that carbon monoxide in aqueous solution can be converted into various simple organic compounds by irradiation with light at 185 nm. The product yields show a specific pH dependence, which can be explained by the properties of the photoproduced primary species. In alkaline solutions, carboxylic acids are formed by a chain reaction mechanism.

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