Photoinduced Transformation of Carbon Monoxide in Aqueous Solution

Hyoung Ryun Park and Nikola Getoff*
Institute for Theoretical Chemistry and Radiation Chemistry,
The University of Vienna, and Ludwig Boltzmann Institute for Radiation Chemistry,
both Währingerstr. 38, A-1090 Wien, Austria

Z. Naturforsch. **43a,** 430–434 (1988); received February 16, 1988

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, $\dot{C}H(OH)_2$, 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 ± 1 °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 $Q(H_2) = 0.40$ [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 ($\varepsilon = 8000$ 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, $\varepsilon = 2160$ 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].

---

* To whom the correspondence should be send.

Reprint requests to Prof. Dr. N. Getoff, Institut für Theoretische Chemie und Strahlenchemie, Universität Wien, Währingerstraße 38, A-1090 Wien/Österreich.

0932-0784 / 88 / 0500-0430 $ 01.30/0. – Please order a reprint rather than making your own copy.

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]:

$$H_2O \rightsquigarrow H_2O^* \rightarrow H + OH, \qquad (1)$$

$$H_2O^* + H_2O^* \rightarrow H_2O^{**} + H_2O, \qquad (2)$$

$$H_2O^{**} \rightarrow e^-_{aq} + H^+_{aq} \text{ (autoionization)}. \qquad (3)$$

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:

$$e^-_{aq} + H^-_{aq} \rightarrow H \quad (k = 2.3 \times 10^{10}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}\ [18]), \qquad (4)$$

$$H + OH^-_{aq} \rightarrow e^-_{aq} \ (k = 1.8 \times 10^7\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}\ [19]). \qquad (5)$$

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} 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 carboxlic acids yield at pH > 10; their total quantum yield is exceeding unity at pH 13.

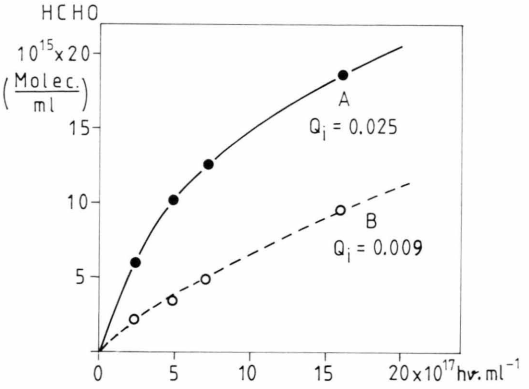


Fig. 1. Formation of formaldehyde at pH = 2 (A) and 7 (B) by reduction of CO in aqueous solution as a function of u.v.-dose at 20 ± 1 °C.

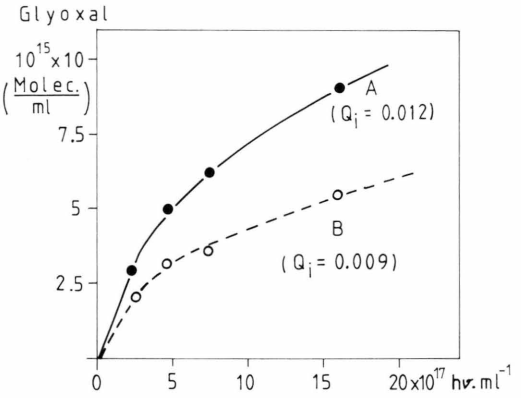


Fig. 2. Formation of glyoxal at pH = 2 (A) and 7 (B) by reduction of CO in aqueous solution as a function of u.v.-dose at 20 ± 1 °C.

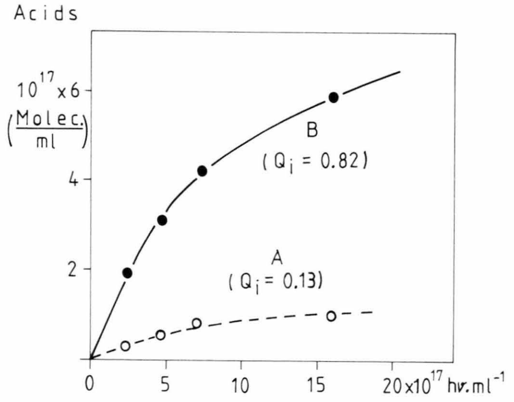
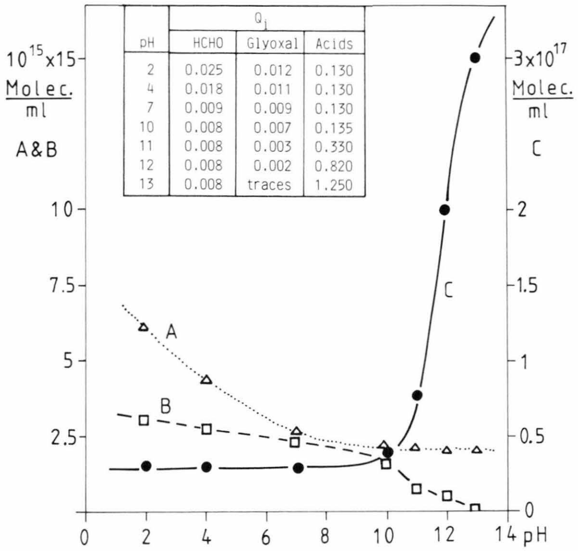


Fig. 3. Total yield of carboxylic acids produced from CO in aqueous solution at 20 ± 1 °C as a function of u.v.-dose at pH = 7 (A) and 12 (B).



pH	Q_i		
	HCHO	Glyoxal	Acids
2	0.025	0.012	0.130
4	0.018	0.011	0.130
7	0.009	0.009	0.130
10	0.008	0.007	0.135
11	0.008	0.003	0.330
12	0.008	0.002	0.820
13	0.008	traces	1.250

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

A) Acid and Neutral Solutions

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

$$\mathrm{CO + H \longrightarrow HCO} \tag{6}$$
$$(k = 3.8 \times 10^8\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}\ [9]),$$

$$\mathrm{2\,HCO \longrightarrow CO + HCHO}\ \text{(formaldehyde)} \tag{7a}$$
$$\longrightarrow \mathrm{(HCO)_2}\ \text{(glyoxal)}, \tag{7b}$$

$$\mathrm{CO + OH \longrightarrow COOH} \tag{8}$$
$$(k = 8.3 \times 10^8\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}\ [1]),$$

$$\mathrm{2\,COOH \longrightarrow CO_2 + HCOOH}\ \text{(formic acid)} \tag{9a}$$
$$\longrightarrow \mathrm{(COOH)_2}\ \text{(oxalic acid)} \tag{9b}$$
$$(2k = 2.0 \times 10^9\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}\ [20]),$$

$$\mathrm{\dot{C}OOH \rightleftharpoons \dot{C}OO^- + H^+}$$
$$(\mathrm{p}K_\mathrm{a} = 2.8\ [21];\ 2.7\ [22]). \tag{10}$$

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

$$\mathrm{2\,COO^- \rightarrow (COO^-)_2}$$
$$(2k = 1.26 \times 10^9\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}\ [20])$$
$$(2k = 1 \times 10^9\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}\ [8]). \tag{11}$$

In addition to the formic and oxalic acids, glyoxalic acid is also produced by combination of HCO and COOH (or $\mathrm{CO_2^-}$) transients, e.g.:

$$\mathrm{HCO + COOH \rightarrow HCO \cdot COOH}\ \text{(glyoxalic acid)}. \tag{12}$$

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

$$\mathrm{HCO + H \rightarrow HCHO}, \tag{13}$$
$$\mathrm{HCO + OH \rightarrow HCOOH}, \tag{14}$$
$$\mathrm{COOH + H \rightarrow HCOOH}, \tag{15}$$
$$\mathrm{COOH + OH \rightarrow CO_2 + H_2O}. \tag{16}$$

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.

$$\mathrm{HCHO + H \longrightarrow H\dot{C}O + H_2} \tag{17}$$
$$(k = 5 \times 10^6\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}\ [23]),$$

$$\mathrm{HCHO + OH \longrightarrow H\dot{C}O + H_2O} \tag{18}$$
$$(k = 2 \times 10^9\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}\ [24]),$$

$$\mathrm{HCHO + \dot{C}OOH \longrightarrow \dot{C}H_2OH + CO_2}, \tag{19a}$$
$$\longrightarrow \mathrm{H\dot{C}O + HCOOH} \tag{19b}$$

$$\mathrm{2\,\dot{C}H_2OH \longrightarrow HCHO + CH_3OH}\ \text{(methanol)} \tag{20a}$$
$$\longrightarrow \mathrm{(CH_2OH)_2}\ \text{(glycol)} \tag{20b}$$
$$2k = 1.9 \times 10^9\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}\ [25].$$

In analogy to HCHO (reactions (17) and (18)) also glyoxal and carboxylic acids can be decomposed by attack of H, OH and other intermediated occuring 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 photoproducts 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]:

$$\mathrm{HCO + H_2O \rightleftharpoons HC(OH)_2}. \tag{21}$$

In a related study on photoinduced degradation of formaldehyde [28] it has been shown that the hydrated formyl radicals, $\mathrm{HC(OH)_2}$, tend to disproportionate to formic acid and hydrated formaldehyde, whereas hydrated glyoxal does not arise:

$$2\dot{C}H(OH)_2 \longrightarrow HCOOH + CH_2(OH)_2 \qquad (22\,a)$$

$$\hphantom{2\dot{C}H(OH)_2} \searrow (CH(OH)_2)_2\,. \qquad (22\,b)$$

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 ($\varepsilon = 3600\,dm^3\,mol^{-1}\,cm^{-1}$ [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

$$OH^-_{aq} \rightsquigarrow (OH^-_{aq})^* \rightarrow OH + e^-_{aq} \qquad (23)$$

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:

$$OH \rightleftharpoons \dot{O}^-_{aq} + H^+ \; (pK = 11.9\,[30])\,, \qquad (24)$$

$$CO + \dot{O}^-_{aq} \rightarrow COO^- \; (k = 3\times10^8\,dm^3\,mol^{-1}\,s^{-1}\,[25])\,. \qquad (25)$$

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 soltuions. Reaction (23) is also responsible for the increase of e^-_{aq} yield, hence

$$CO + e^-_{aq} \rightarrow \dot{C}O^-_{aq}\, (k = 1\times10^9\,dm^3\,mol^{-1}\,s^{-1}\,[4])\,. \qquad (26)$$

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

$$HCOOH^- + OH^-_{aq} \rightarrow HCOO^- + e^-_{aq}\,, \qquad (27)$$

$$HCOO^- + OH \rightarrow \dot{C}OO^- + H_2O \qquad (28)$$

$$(k = 2.5\times10^9\,dm^{-1}\,mol^{-1}\,s^{-1}\,[31])\,.$$

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

$$HCO + COO^- \rightarrow HCO\,COO^-\,. \qquad (29)$$

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:

$$H\dot{C}OOH^- \overset{-H_2O}{\rightleftharpoons} \dot{C}O^- \overset{+H^+}{\rightleftharpoons} \dot{C}HO \overset{+H_2O}{\rightleftharpoons} \dot{C}H(OH)_2\,. \qquad (30)$$

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.

[1] Y. Raef and A. J. Swallow, Trans. Faraday Soc. **59,** 1631 (1963).

[2] J. Holian, G. Scholes, and J. J. Weiss, Nature **191,** 1386 (1961).

[3] N. Getoff and D. Seitner, Z. Phys. Chem. (NF) **51,** 27 (1966).

[4] D. Seitner and N. Getoff, Z. Phys. Chem. **66,** 22 (1969).

[5] D. Seitner and N. Getoff, Monatsh. Chem. **100,** 1868 (1969).

[6] E. P. Kalyazin and N. M. Baranova, Neftekhimiya (russ.) **4,** 275 (1964).

[7] R. Marz and C. Chachaty, J. Chim. Phys. **58,** 527 (1961).

[8] J. P. Keene, Y. Raef, and A. J. Swallow, p. 99 in: Pulse Radiolysis, eds. M. Ebert, J. P. Keene, A. J. Swallow, and J. H. Baxendale, Academic Press, London 1965.

[9] N. Getoff and H. P. Lehmann, Int. J. Radiat. Phys. Chem. **2,** 91 (1970).

[10] W. Zich and N. Getoff, Monatsh. Chem. **100,** 1745 (1969).

[11] N. Getoff, Monatsh. Chem. **99,** 136 (1968).

[12] N. Getoff and G. O. Schenck, Photochem. Photophys. **8,** 167 (1968).

[13] C. von Sonntag and H. P. Schuchmann, Adv. Photochem. **10,** 59 (1977).

[14] T. Nasch, Biochem. J. **55,** 418 (1958).

[15] T. Banks, C. Vaughn, and L. Marshall, Analyt. Chem. **27,** 1348 (1955).

[16] R. D. Hartley and G. I. Lawson, J. Chromatog. **7,** 69 (1962).

[17] F. S. Dainton and P. Fowles, Proceed. Roy. Chem. Soc. **A 287,** 295 (1965).

[18] L. M. Dorfman and I. A. Taub, J. Amer. Chem. Soc. **85,** 2370 (1963).

[19] M. S. Matheson and J. Rabani, J. Phys. Chem. **69,** 1324 (1965).

[20] N. Getoff and F. Schwörer, unpubl. data.

[21] F. Gütlbauer and N. Getoff, Z. Phys. Chem. (NF) **5,** 225 (1966).

[22] D. Jez and N. Getoff, unpublished results.

[23] J. H. Baxendale and D. Smithies, Z. Phys. Chem. (NF) **7,** 242 (1956).

[24] E. J. Hart, J. K. Thomas, and S. Gordon, Radiat. Res. Suppl. **4,** 74 (1964).

[25] N. Getoff, unpublished results.

[26] J. Walker, Formaldehyde, 3 ed. Reinhold Pub. Comp., New York 1964.

[27] R. Bieber and G. Trümpler, Helv. Chim. Acta **30,** 1860 (1947).

[28] H. R. Park and N. Getoff, J. Photochem. Photob., in print.

[29] F. S. Dainton and P. Fowles, Proc. Roy. Chem. Soc. **A-287,** 312 (1965).

[30] J. W. T. Spinks and R. J. Woods, An Introduction to Radiation Chemistry, John Wiley & Sons, New York 1976.

[31] J. K. Thomas, Faraday Soc. **61,** 702 (1965).