

Radiation Induced Incorporation of CO in Pure and Aqueous Methanol

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Pure and aqueous methanol were used for radiation induced incorporation of CO at elevated pressure (up to 15 bar). The initial yields (G_i) of the main products in pure methanol under 15 bar CO and 1 bar N_2O were found to be: G_i (formaldehyde) = 3.80 and G_i (glycolic aldehyde) = 2.0. For aqueous ($10^{-2} \text{ mol} \cdot \text{dm}^{-3}$) methanol under 15 bar CO (dose: 0.557 kGy, pH = 2): the yields were G (formaldehyde) = 5.44, G (glycolic aldehyde) = 4.0 and G (oxalic acid) = 7.7. At pH = 7 the yields were essentially lower, namely: G (formaldehyde) = 3.2, G (glycolic aldehyde) = 2.0, G (formate) = 3.8 and G (oxalate) = 5.0. Probable reaction-mechanisms for the product formation are discussed.

Based on previous carbonylation experiences of gamma-, electron- and UV-irradiated aqueous methanol under 1 bar CO ($10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ CO) [1–6] the aim of the present work was to investigate this process at elevated CO pressures. Pure methanol as well as aqueous solutions were used for this purpose.

1. Experimental

1.1. Radiation Source and Solution Preparation

A “Gammacell 220” (Atomic Energy of Canada Ltd.) was used as a ^{60}Co - γ -source, having a dose rate of $40 \text{ Gy} \cdot \text{min}^{-1}$ *. The dosimetry was performed by means of a ferrous-copper dosimeter under the same experimental conditions [7].

The applied methanol (p. A. Merck) was freshly distilled under argon atmosphere and kept in absence of air before use. High purity CO (Messer-Griesheim GmbH, Vienna) was used without further purification. The samples (50 ml) of pure or aqueous methanol

were given into an open glass vessel which was fitted in an autoclave (see Figure 1). Prior to irradiation the solutions were deoxygenated by bubbling for 45 min with high purity argon and then saturated with CO at various pressures (1–15 bar).

1.2. Analysis

Aliquots of the irradiated solutions were analyzed by spectrophotometric methods for the yields of formaldehyde [8], glycolic aldehyde [9], glyoxal [10] and oxalic acid [11]. The total yield of the formed carboxylic acids was determined by titration with $10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ NaOH. The individual measurement of the formic acid was achieved by water steam distillation of an aliquot of the solution, followed by reduction with magnesia to formaldehyde in acid solution. By substrating the yield of the priorly measured aldehydes from the obtained total aldehyde amount, the formic acid yield was determined. In addition to this, the GC-method was applied in most cases, as well for the individual determination of glycol and other products. A GC-instrument (Carlo Erba 4160) equipped with split/splitless injector, FID and a 20 m glass capillary column with i.d. 0.32 mm coated with CW 20 M (high polymer carbowax, film thickness 0.2 μm) was used. Hydrogen was applied as carrier gas (flow rate 2.6 ml/min). The injector temperature was 260 °C and that of the column 108 °C. The presented yields are mean values of the data obtained

* 1 Gray (Gy) = $1 \text{ J} \cdot \text{kg}^{-1}$ = 100 rad = $6.24 \times 10^{15} \text{ eV} \cdot \text{g}^{-1}$.

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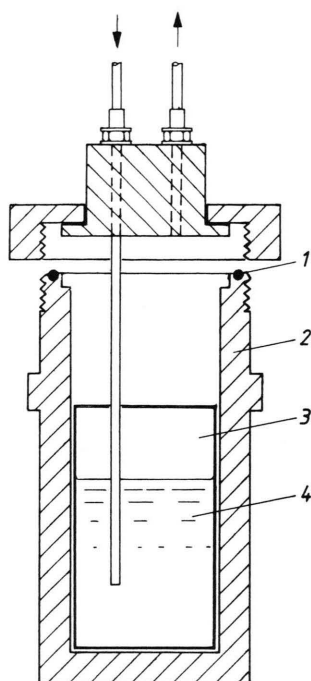


Fig. 1. Cross-section of the autoclave with glass vessels used for the irradiation experiments. (1) Rubber seal ring, (2) stainless steel autoclave, (3) glass vessel and (4) sample solution.

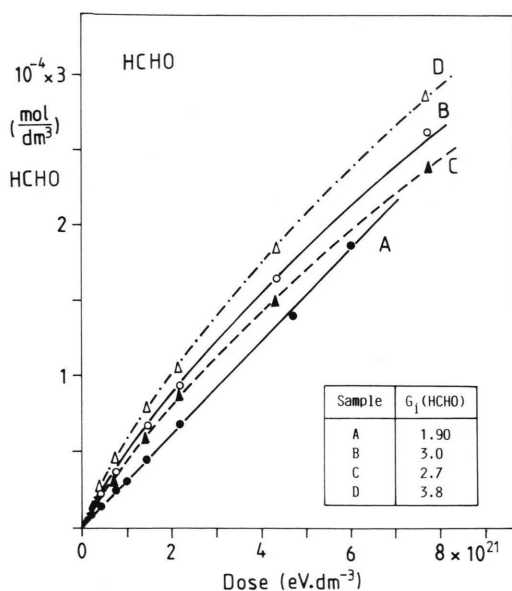


Fig. 2. Radiation induced formation of formaldehyde as a function of the absorbed dose at various CO-concentrations in methanol. (A) Airfree, (B) saturated with 10 bar CO, (C) saturated with 1 bar N_2O and 2 bar CO and (D) 1 bar N_2O and 10 bar CO.

by the various methods, and are expressed as G -values**.

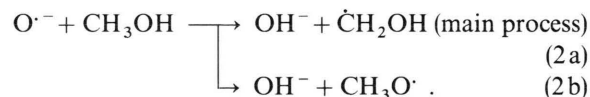
2. Results and Discussion

2.1. Carbonylation of Pure Liquid Methanol

The radiation induced incorporation of CO in methanol is a result of competing reactions between the primary products of methanol radiolysis (see below) and the ability of CO to scavenge H , e_s^- and $\dot{\text{C}}\text{H}_2\text{OH}$. Thereby the carbon monoxide concentration is the determining factor of the process. Based on this fact the formation of the final products resulting from the $\text{CH}_3\text{OH}/\text{CO}$ -system was studied as a function of CO-concentration and absorbed radiation dose. In some series of experiments the solutions were first saturated at room temperature with N_2O ($0.16 \text{ mol} \cdot \text{dm}^{-3}$) [12] as a specific scavenger for e_s^- in order to increase the yield of the $\dot{\text{C}}\text{H}_2\text{OH}$ radicals, since



$$k_1 = 1.3 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad [13],$$



In Fig. 2 the formation of formaldehyde is presented as a function of the absorbed dose in pure methanol as well as in samples saturated with CO under pressure. The obtained initial G -values (G_i) are given in an insert in Figure 2. From the obtained data it is obvious that in the presence of 1 bar* ($0.16 \text{ mol} \cdot \text{dm}^{-3}$) N_2O and 10 bar ($0.09 \text{ mol} \cdot \text{dm}^{-3}$) CO $G_i(\text{HCHO}) = 3.8$ (curve D, Fig. 2), compared to $G_i = 3.0$ (curve B, Fig. 2) in absence of N_2O , but at 10 bar CO. These data indicate the role of N_2O pointed out by reactions (1) and (2). The same conclusion can be drawn from curve C in Fig. 2, where on applying 1 bar N_2O and 2 bar CO $G = 2.7$ was obtained.

The reaction mechanisms taking place under these experimental conditions will be subsequently discussed.

** G -Value = number of produced or decomposed molecules per 100 eV absorbed energy. G_i (initial G -value) is the value before secondary reactions take place. $G = 1$ is equivalent to $1.0364 \times 10^{-7} \text{ mol} \cdot \text{J}^{-1}$.

* 1 atm = 1.013 bar = 101 300 pascal.

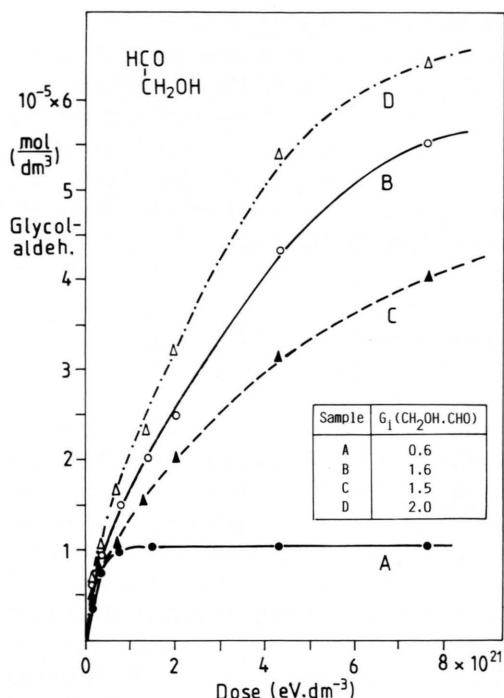


Fig. 3. Formation of glycolic aldehyde as a function of absorbed dose for various CO concentrations in pure methanol. (A) Airfree, (B) saturated with 10 bar CO, (C) saturated with 1 bar N_2O and 2 bar CO and (D) saturated with 1 bar N_2O and 10 bar CO.

The yields of glycolic aldehyde as a function of dose resulting from the same systems mentioned above are shown in Figure 3. The highest G -value is again obtained in a solution containing 1 bar N_2O and 10 bar CO. Obviously, with increasing the concentration of CO and hence that of the $\dot{\text{HCO}}$ radicals the yield of the glycolic aldehyde is also increased. The presence of N_2O , leading to an enhanced yield of $\dot{\text{CH}}_2\text{OH}$ (see reactions (1) and (2)), contributes essentially to relatively high yields of glycolic aldehyde.

It is of interest to be mentioned that in all $\text{CH}_3\text{OH}/\text{CO}$ systems the formation of glyoxal and glycol was not observed. The G -values of the major products determined in the absence and in the presence of CO are summarized in Table 1 and compared with previous data.

The product yields in Table 1 show that the previously observed G_i -values of H_2 , HCHO and glycol a radiolytic products of pure methanol are in good agreement with the present ones. Further, at sufficient CO concentration in methanol the $\dot{\text{CH}}_2\text{OH}$ radicals

Table 1. G_i -value of some major final products formed in: a) airfree methanol, b) saturated with 1 bar ($0.16 \text{ mol} \cdot \text{dm}^{-3}$) N_2O and (c) 1 bar N_2O and 10 bar ($0.019 \text{ mol} \cdot \text{dm}^{-3}$) CO.

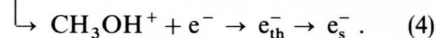
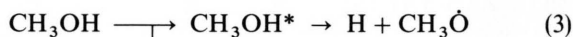
| Major final products | (a) Airfree pure methanol | (b) 1 bar N_2O in pure methanol | (c) 1 bar N_2O and 10 bar CO in pure methanol (this work) |
|---|-----------------------------|---|---|
| H_2 | 5.8 [27] — | 3.35 [27] 3.30 this work | not measured |
| HCHO | 1.85 [27] 1.90 this work | 2.60 [27] 2.70 this work | — 3.80 |
| $(\text{CH}_2\text{OH})_2$ | 3.52 [27] 3.6 this work | 3.25 [27] 3.34 this work | traces — |
| $\text{CH}_2\text{OH} \cdot \text{CHO}$ | 0.78 [13]* 0.6 this work | — — | 2.0 — |

* Pure methanol was saturated with CO ($0.01 \text{ mol} \cdot \text{dm}^{-3}$).

are practically scavenged by $\dot{\text{CHO}}$ and other species in the bulk of the solution, so that the formation of glycol is suppressed.

2.2. Reaction Mechanisms in Pure Methanol Systems

The radiation energy absorbed in methanol causes excitation and ionization processes which lead to the formation of numerous primary species, see e.g. [13–16],

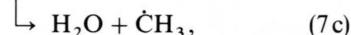
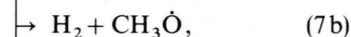
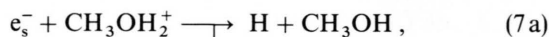
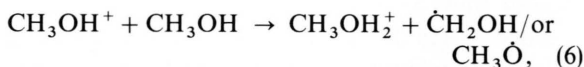


It was very recently proven [15] that the $\text{CH}_3\dot{\text{O}}$ radicals are primarily formed in addition to H-atoms and thermalized electrons (e_{th}^-), which are subsequently solvated (e_s^-) within a few ps. The $\text{CH}_3\dot{\text{O}}$ radicals are scavenged by the CH_3OH molecules in the ground state and converted into $\dot{\text{CH}}_2\text{OH}$ transients:



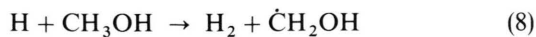
$$k_5 = 2.6 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} [17].$$

Further more important consecutive reactions are:



$$k_7 = 5.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} [18].$$

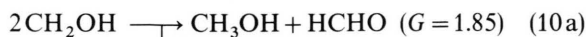
The species H, e_s^- , and $\dot{\text{C}}\text{H}_2\text{OH}$ are involved in additional processes:



$$k_8 = 3.2 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} [19],$$



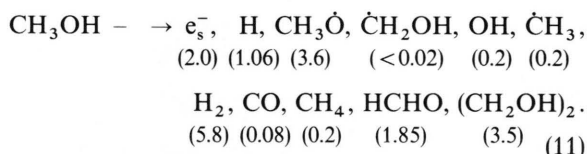
$$k_9 = 1.1 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} [19],$$



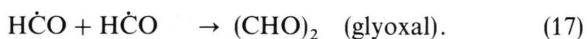
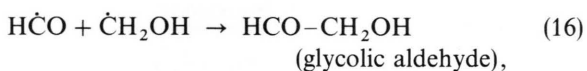
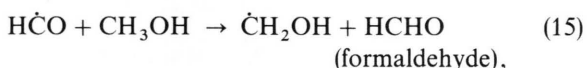
$$k_{10a} = 1.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-2} \text{ s}^{-1}$$

$$\text{and } k_{10b} = 1.7 \times 10^9 \text{ dm}^2 \text{ mol}^{-1} \text{ s}^{-1} [13, 19].$$

As a result of these and other reactions of minor interest a number of radicals and molecular products are formed [14–16]; the *G*-values of the primary products are given in brackets:

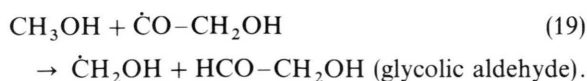


In the presence of CO the following secondary radicals can be formed:



As already mentioned, the formation of glyoxal was not observed, because reaction (17) cannot compete with reactions (15) and (16), where reaction (15) is predominant. Reaction (10a), formation of formaldehyde as well as (10b), generation of glycol are also suppressed by reaction (16).

Based on the obtained results it is obvious, that at higher CO-concentrations CO can also react to some extent with $\dot{\text{C}}\text{H}_2\text{OH}$ in competition to reaction (16):



Based on the reaction steps (18) and (19), a chain-reaction is conceivable in addition to reaction (16) for the formation of glycolic aldehyde. However, the obtained G_i (glycolic aldehyde) = 2.0 in the case of 1 bar and 10 bar CO is indicating that reaction (18) under the given conditions is not of essential importance. Hence, the main products of the methanol/CO system are formaldehyde and glycolic aldehyde (Table 1).

2.3. Carbonylation of Aqueous Methanol at Elevated CO-pressure

As previously reported [1] the radiation induced carbonylation of aqueous methanol (10^{-5} to $25 \text{ mol} \cdot \text{dm}^{-3}$; 1 bar CO, pH-range: -0.3 to 12) at room temperature depends strongly on the pH and the methanol concentration. Using aqueous $10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ CH_3OH saturated with 1 bar ($1 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) CO the highest G_i ($\text{CH}_2\text{OH} \cdot \text{CHO}$) = 1.75 was observed at pH = 0.5. Studying the effect of methanol concentration on the glycolic aldehyde yield in the presence of 1 bar CO, an unusually shaped curve was obtained at pH = 5.4 and a dose of 4.13 kGy. It passed a maximum at $2 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ CH_3OH ($G = 0.51$) a minimum at $3 \text{ mol} \cdot \text{dm}^{-3}$ CH_3OH ($G = 0.14$) and reached its highest value using pure methanol [1]. This was explained by the competition reactions involved in the carbonylation process of aqueous methanol.

It was now of interest to study to some extent the role of the CO concentration (up to 15 bar) in aqueous methanol in respect to the glycolic aldehyde formation. Hence, an aqueous $10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ methanol solution at pH = 2 and 7 was irradiated (dose: 57.7 Gy) in the presence of CO at various pressures.

The yield of formaldehyde, glycolic aldehyde, formic acid and oxalic acid were determined and are presented in Figure 4.

As to be expected at pH = 2 formaldehyde is also formed by the radiolysis of deoxygenated $10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ methanol. With increasing the CO-concentration (1 to 15 bar CO) also a linear increase of the formaldehyde yield is found. The same effect is observed for the formation of glycolic aldehyde in respect to the increased CO concentration. The course of the oxalic acid curve is up to 5 bar CO rather steep, but above this range it is nearly proportional to the CO-concentration. The yields of formaldehyde, glycolic aldehyde as well as of formate and oxalate

Table 2. *G*-values of formaldehyde, glycolic aldehyde, formic acid and oxalic acid formed in 10^{-2} mol · dm⁻³ methanol at various CO-pressure at pH=2 and 7. Applied dose: 0.557 kGy.

| | <i>G</i> -values at CO pressure of: | | | |
|-------------------|-------------------------------------|-------|--------|--------|
| | 1 bar | 5 bar | 10 bar | 15 bar |
| pH=2 | | | | |
| Formaldehyde | 1.76 | 2.85 | 4.5 | 5.44 |
| Glycolic aldehyde | 0.34 | 1.34 | 2.5 | 4.0 |
| Oxalic acid | 1.5 | 3.85 | 6.0 | 7.7 |
| pH=7 | | | | |
| Formaldehyde | 0.35 | 1.0 | 2.2 | 3.2 |
| Glycolic aldehyde | 0.24 | 0.83 | 1.5 | 2.0 |
| Formate | 0.54 | 1.25 | 2.7 | 3.8 |
| Oxalate | 0.7 | 1.8 | 3.7 | 5.0 |

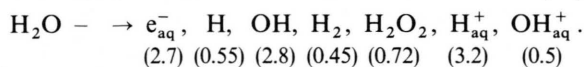
observed at pH = 7, resulting as products of 10^{-2} mol · dm⁻³ methanol under the same experimental conditions increase practically linearly with the applied CO-pressure (insert, Figure 4).

For a better illustration of the pH-effect, the *G*-values of the products presented in Fig. 4 were calculated and summarized in Table 2. Obviously, the yields obtained at pH = 2 are essentially higher than those found at pH = 7. A similar observation has previously been made on carboxylation of aqueous methanol using 1 bar CO [1].

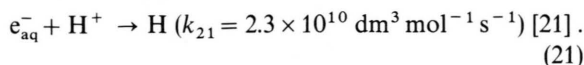
It is also of interest to point out that the formation of formaldehyde, glycolic aldehyde, formic and oxalic acids were previously observed in the radiation induced oxidation of methanol in the presence of air as well as of pure oxygen up to 5 bar [20].

2.4. Reaction Mechanisms of the CO-incorporation in Aqueous Methanol

The radiolysis of water is well understood and can be represented by the brutto reaction (20), where the *G*-values of the primary species at pH = 7 are given in brackets [16]:



In acid solution (pH = 2) e_{aq}^- is converted into H-atom:



This process is to some extent in competition with reaction (22), especially at higher CO-pressures in the

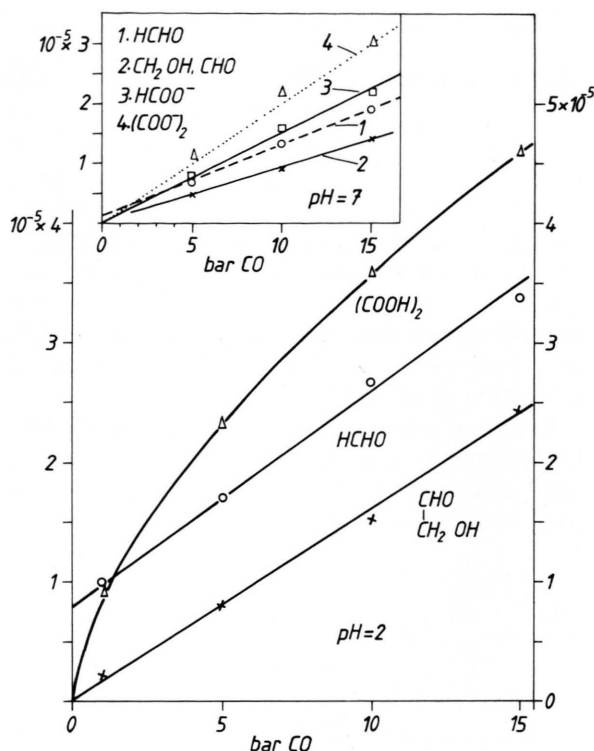
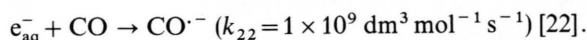
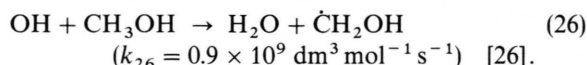
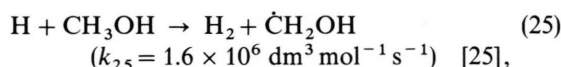
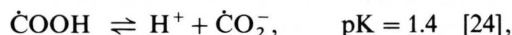
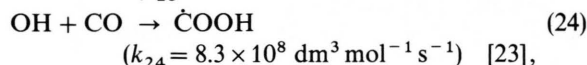
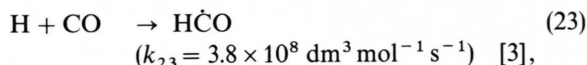


Fig. 4. Radiation induced formation of form- and glycolic aldehydes as well as of form- and oxalic acids in aqueous 10^{-2} mol · dm⁻³ methanol at various CO-concentrations at pH = 2 and 7 (see insert). Absorbed: 0.557 kGy.

aqueous methanol: (22)



The remaining species (H, OH) react with both, methanol and CO:



The formation of the observed products in acid solution (pH = 2) can be explained by the reactions





No glyoxal $(\text{HCO})_2$ was found because the $\dot{\text{HCO}}$ radicals are scavenged according to the reactions (27) and (28). Since only traces of glycol were found, it seems that the dimerisation and disproportion of $\dot{\text{CH}}_2\text{OH}$ do not take place under the given conditions (see reactions (10a) and (10b)).

In neutral solutions the $\dot{\text{CO}}_2^-$ -radicals are involved in the formation of formate and oxalate. It should be mentioned that glycolic acid was also detected, but its yield was not determined.



It might be noticed that in alkaline aqueous solution CO-species are leading to a chain-reaction, resulting in the formation of formate with $G = 44$ [23]:



Further experiments in this respect are in progress.

3. Conclusion

The radiation induced incorporation of CO at elevated pressure (up to 15 bar) in pure as well as aqueous methanol was studied in view of a future utilization of CO. The yields of the final products: formaldehyde, glycolic aldehyde, formic and oxalic acids were measured. In aqueous methanol solutions, in addition to the CO-concentration the pH is a determining factor of the process.

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