Radiation Induced Oxidation of Methanol

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The radiolysis of methanol in the presence of air as well as of pure oxygen (1 to 5 atm) was investigated. The yields of the major products: carboxylic acids (by far predominantly formic acid), oxalic acid, formaldehyde and glycolaldehyde were determined as a function of the absorbed dose. In addition small amounts ($G \leq 0.05$) of glyoxal, glyoxalic acid and glycolic acid were also detected. Based on the results a possible reaction mechanism is presented.

Introduction

The radiolysis of pure methanol in the presence of oxygen has been the subject of a few papers only [1–3]. As major products were obtained formaldehyde, formic acid, peroxides and hydrogen. With increasing the concentration of oxygen the yield of glycol is reduced up to nil. The rate constant (k) for the reaction of solvated electrons with oxygen is very high, $k(e_s^- + O_2) = 2.0 \times 10^{10}$ dm³ mol⁻¹ s⁻¹ [4]. Just so react the H-atoms in acidified methanol (0.5 vol.% aqueous 1 mol dm⁻³ HClO₄), $k(H + O_2 \rightarrow HO_2) \sim 2 \times 10^{10}$ dm³ mol⁻¹ s⁻¹ [5]. The resulting peroxyradicals show absorption maxima at 240 nm (assigned to $\dot{O}_2^-$ and $H\dot{O}_2$) and 265 nm (assumed to be $\dot{O}_2CH_2OH$) [4].

The aim of the present work was to investigate the radiation induced oxidation of pure liquid methanol in the presence of air as well as of oxygen at various concentrations. The yields of the final products were determined as a function of dose.

Experimental

Radiation Source and Dosimetry

A "Gammacell 220" (Atomic Energy of Canada Ltd., dose rate 30 Gy/min) [1] was used as a radiation source. The dosimetry was performed by modified Fricke (ferrous sulfate) as well as by ceric sulfate dosimeters [6]. The determined dose was corrected for pure methanol.

Preparation of Solutions

The methanol was freshly distilled under argon before use. The samples (30–50 ml) were either irradiated in the presence of air or put into open pyrex-glass vessels mounted in a stainless steel autoclave, having an inlet (reaching in the solution) and outlet valve. In the last case the samples were first saturated with high purity oxygen (99.99%) for about 30 min, and than the desired pressure (1–5 atm O₂) [2] was applied until equilibrium. The solutions were irradiated at various doses at the same dose rate.

Analysis

Immediately after irradiation aliquote parts of the samples were diluted with distilled water and analyzed by means of spectrophotometrical methods. Formaldehyde was specifically determined by the method by Hantzsch described by Nash [7] measuring the optical density (OD) of the solution at 412 nm ($\varepsilon = 7850$ dm³ mol⁻¹ cm⁻¹). Glycol aldehyde was converted to osazone by means of 2,4-dinitrophenylhydrazine [8] after a modified method [9], and the yield was measured at 562 nm ($\varepsilon = 49\,800$ dm³ mol⁻¹ cm⁻¹). The corresponding osazone-compounds resulting at the same time from formaldehyde (absorbs at 430 nm) and that from glyoxal (570 nm) are taken into account. The formaldehyde yield observed by both methods

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[1] 1 krad = 10 Gy (Gray) = 6.24×10^{16} eV/g.

[2] 1 atm = 101 300 Pa = 1.013 bar.

was compared. A separate determination of glyoxal ensued also by using 1,2-dianilinoethane as reagent ($\lambda = 600$ nm) [10, 11]. It was established that primarily only small amounts of glyoxal ($G \leq 0.05$) were formed; hence it was not further taken into consideration.

The major products resulting from the methanol oxidation were carboxylic acids. Their total yield was determined by titration with 0.01 mol dm^{-3} NaOH. Using paper chromatography [12], it was found that formic acid was the prevailing part, followed by oxalic acid and very small amounts of glyoxylic and glycolic acids ($G \leq 0.05$). The specific yield of oxalic acid was determined as copper-benzidine complex [13].
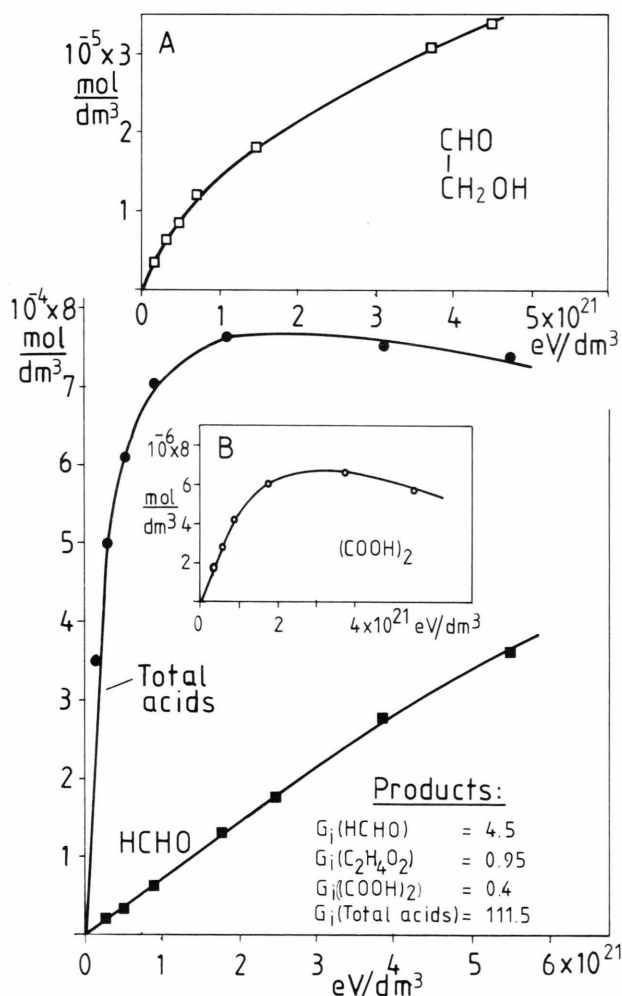

Fig. 1. Final products formed by methanol radiolysis in the presence of air as functions of absorbed dose.
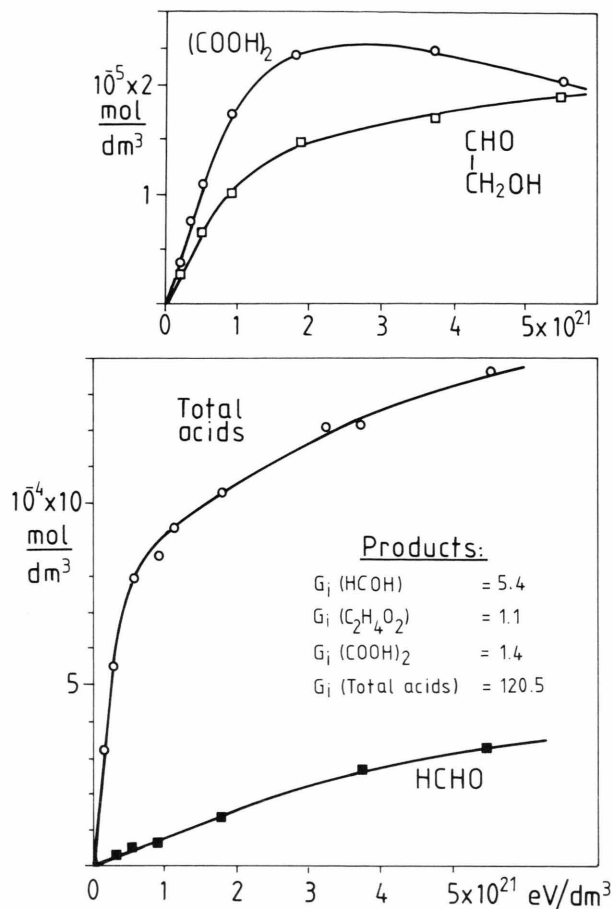

Fig. 2. Final products resulting from methanol radiolysis in the presence of 1 atm O$_2$ (0.0114 mol/dm^3 O$_2$) as functions of absorbed dose.

Results and Discussion

The yield of the main products resulting from air saturated methanol is presented in Fig. 1 as a function of the absorbed dose. Obviously, the yield of the total acids is by far the highest, reaching an initial G-value [3], $G_i = 111.5$. This indicates that a chain reaction is involved in the process of their formation. The observed plateau of the acids yield is falling off at high doses ($> 4 \times 10^{21}$ eV/dm^3). This is a consequence of the enhanced oxygen consumption. Formaldehyde is appearing as the second main product ($G_i = 4.5$) showing a nearly linear yield-dose curve. The formation of the

[3] G-value = number of transformed molecules per 100 eV absorbed energy. G_i = initial G-value, calculated before secondary reactions take place. For conversion in SI-units multiply G_i by 0.10364 to obtain the yield in µmol J^{-1}.
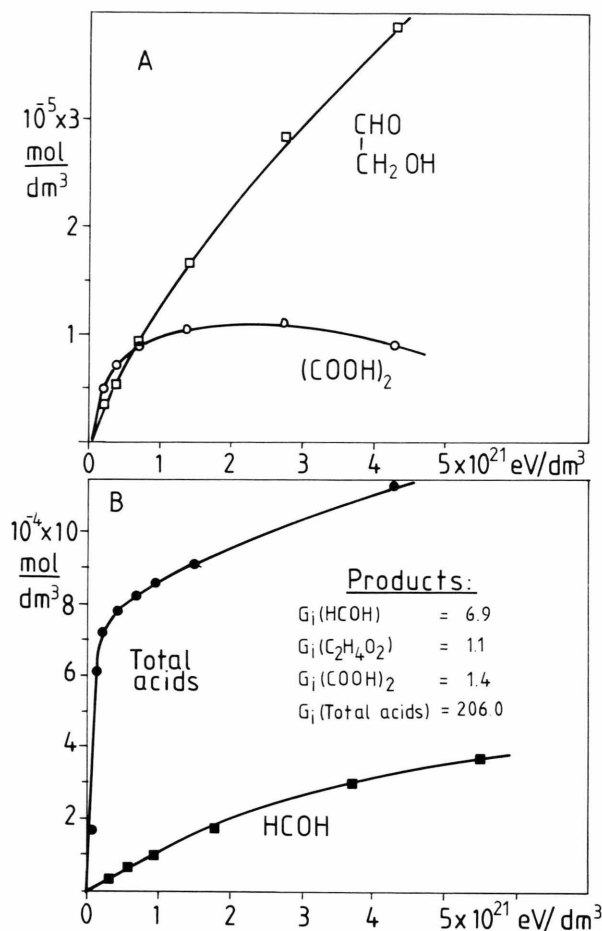
Fig. 3. Final products formed by radiolysis of methanol in the presence of 5 atm O_2 (0.057 mol/dm³ O_2) as functions of absorbed dose.

two other products, glycol aldehyde ($G_i = 0.95$; insert A, Fig. 1) and oxalic acid ($G_i = 0.4$; insert B, Fig. 1) are much more sensitive to the available oxygen concentration.

By saturating methanol with 1 atm pure oxygen (0.0114 mol/dm³ O_2) the yields of the final products are increased. Figure 2 represents the course of their dose-yield curves. In this case G_i(total acids) = 120.5. The corresponding curve shows a bend at a dose at about 0.5×10^{21} eV/dm³, but no plateau and no decrease above that dose (compare with Figure 1). The formation run of formaldehyde ($G_i = 5.4$), glycol aldehyde ($G_i = 1.1$) and oxalic acid ($G_i = 1.4$) is rather similar to those observed in methanol saturated with air (Figure 1).
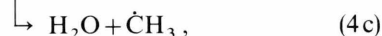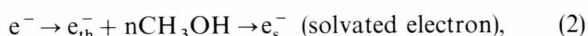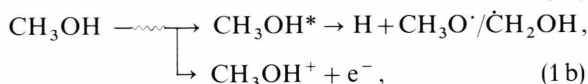
A further increase of the initial oxygen concentration in methanol to 5 atm (0.057 mol/dm³ O_2) leads to

a rather high enhancement of the carboxylic acids yield ($G_i = 206$), but to a small one of formaldehyde ($G_i = 6.9$). The yields of glycol aldehyde ($G_i = 1.1$) and oxalic acid ($G_i = 1.4$) remain the same as before. The experimental data are illustrated in Figure 3. Based on these facts it can be assumed that both last mentioned products are formed as a result of secondary processes.
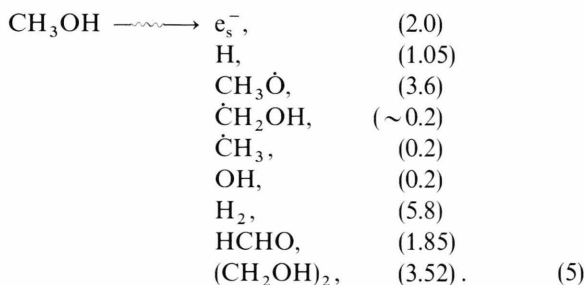
Radiolysis of Airfree Methanol

For a better understanding of the subject matter, the radiolysis of pure, airfree methanol should first be reviewed. There are a number of processes initiated by irradiation [4, 14–16]:

$$CH_3OH \longrightarrow\hspace{-1.2em}\sim\sim\sim\hspace{0.4em} \begin{cases} CH_3OH^* \rightarrow H + CH_3O^{\cdot}/\dot{C}H_2OH, & \text{(1a)} \\ CH_3OH^+ + e^-, & \text{(1b)} \end{cases}$$

$$e^- \rightarrow e_{th}^- + nCH_3OH \rightarrow e_s^- \text{ (solvated electron)}, \quad \text{(2)}$$

$$CH_3OH^+ + CH_3OH \rightarrow CH_3OH_2^+ + \dot{C}H_2OH, \quad \text{(3)}$$

$$CH_3OH_2^+ + e_s^- \longrightarrow \begin{cases} H + CH_2OH, & \text{(4a)} \\ H + CH_3\dot{O}, & \text{(4b)} \\ H_2O + \dot{C}H_3, & \text{(4c)} \end{cases}$$

$$k_4 = 5.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1} \quad [17].$$

According to results obtained by ESR-spin trapping technique, Shiotani et al. [18, 19] predict that methoxy radicals ($CH_3O^{\cdot}$) and H-atoms are the primary radiolytic products of methanol. On the other hand, Sargent and Gardy [20] and Sargent [21], using the same method, concluded that both species, $\dot{C}H_3O$ ($G = 2.5$) and $\dot{C}H_2OH$ ($G = 1.0$) are formed as primary transients. Using triethylsilane as scavenger for both species, $CH_3\dot{O}$ and $\dot{C}H_2OH$, Getoff et al. [22] concluded that $CH_3\dot{O}$ radical is practically the primary product of methanol radiolysis. The yield of $\dot{C}H_2OH$ species is rather low ($G \sim 0.2$). Based on the literature data, the brutto reaction for the methanol radiolysis can be given as follows:

$$CH_3OH \longrightarrow\hspace{-1.2em}\sim\sim\sim\hspace{0.4em} \begin{array}{ll} e_s^-, & (2.0) \\ H, & (1.05) \\ CH_3\dot{O}, & (3.6) \\ \dot{C}H_2OH, & (\sim 0.2) \\ \dot{C}H_3, & (0.2) \\ OH, & (0.2) \\ H_2, & (5.8) \\ HCHO, & (1.85) \\ (CH_2OH)_2, & (3.52). \end{array} \quad \text{(5)}$$

In addition, small amounts of CO ($G = 0.13$) and CH_4 ($G = 0.65$) were also found [14, 15]. The number given in brackets indicate the corresponding G-values.
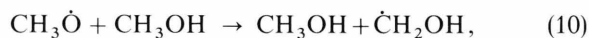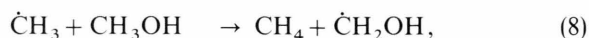
The above mentioned transients are involved in the following processes:

$$H + CH_3OH \rightarrow H_2 + CH_2OH, \tag{6}$$
$$k_6 = 3.2 \times 10^6 \, dm^3 \, mol^{-1} s^{-1} \quad [4],$$

$$e_s^- + CH_3OH \rightarrow H + CH_3\dot{O}^-, \tag{7}$$
$$k_7 = 1.1 \times 10^4 \, dm^3 \, mol^{-1} s^{-1} \quad [4],$$

$$\dot{C}H_3 + CH_3OH \rightarrow CH_4 + \dot{C}H_2OH, \tag{8}$$

$$OH + CH_3OH \rightarrow H_2O + \dot{C}H_2OH, \tag{9}$$

$$CH_3\dot{O} + CH_3OH \rightarrow CH_3OH + \dot{C}H_2OH, \tag{10}$$
$$k_{10} = 2.6 \times 10^5 \, dm^3 \, mol^{-1} s^{-1}, \quad [23],$$

$$2\dot{C}H_2OH \longrightarrow CH_3OH + HCHO, \tag{11a}$$
$$\longrightarrow (CH_2OH)_2, \tag{11b}$$
$$k_{11} = 2.8 \times 10^9 \, dm^3 \, mol^{-1} s^{-1} \quad [4].$$

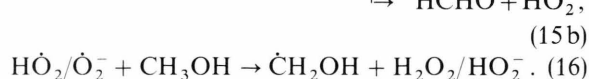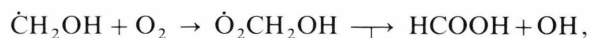*Methanol Radiolysis in the Presence of Oxygen*

Most of the primary methanol products discussed above are reacting with molecular oxygen and result in peroxy-radicals which give rise for the formation of various products:
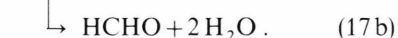
$$e_s^- + O_2 \rightarrow \dot{O}_2^-, \tag{12}$$
$$k_{12} = 2 \times 10^{10} \, dm^3 \, mol^{-1} s^{-1} \quad [4],$$

$$H + O_2 \rightarrow H\dot{O}_2, \tag{13}$$
$$k_{13} \sim 2 \times 10^{10} \, dm^3 \, mol^{-1} s^{-1} \quad [5],$$

$$H\dot{O}_2 \rightleftharpoons H^+ + \dot{O}_2^-, \tag{14}$$

$$\dot{C}H_2OH + O_2 \rightarrow \dot{O}_2CH_2OH \longrightarrow HCOOH + OH, \tag{15a}$$
$$\longrightarrow HCHO + H\dot{O}_2, \tag{15b}$$

$$H\dot{O}_2 / \dot{O}_2^- + CH_3OH \rightarrow \dot{C}H_2OH + H_2O_2/HO_2^-. \tag{16}$$

H_2O_2 is oxidizing methanol relatively slowly, initiating further reaction steps:

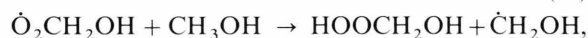$$H_2O_2 + CH_3OH \longrightarrow \dot{C}H_2OH + OH + H_2O, \tag{17a}$$
$$\longrightarrow HCHO + 2H_2O. \tag{17b}$$

The OH radicals are consumed by reaction (9) and the $H\dot{O}_2$ species likewise, reaction (16), both resulting in $\dot{C}H_2OH$ transients. The peroxy-radicals, $\dot{O}_2CH_2OH$,

can initiate further reaction steps, which can be rather essential in the propagation of the above chain reactions, (15a) and (16):

$$2\dot{O}_2CH_2 \longrightarrow 2 HCOOH + H_2O_2, \tag{18a}$$
$$\longrightarrow 2 HCHO + H_2O_2 + O_2 \tag{18b}$$

or:
$$\tag{19}$$

$$\dot{O}_2CH_2OH + CH_3OH \rightarrow HOOCH_2OH + \dot{C}H_2OH,$$
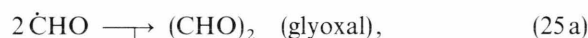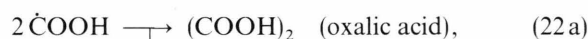
$$HOOCH_2OH \rightarrow HCOOH + H_2O. \tag{20}$$
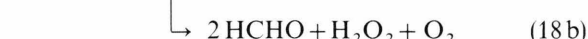
In this case preference is given to reactions (18a), (19) and (20) because of the very high yield of formic acid compared to that of formaldehyde (see Figs. 1, 2, 3).

In addition to reactions (12)–(20), also reaction steps caused by the attack of radicals in the bulk ($R\cdot$) on the final products can take place, e.g.

$$HCOOH + R\cdot \rightarrow RH + \dot{C}OOH/HCO\dot{O}, \tag{21}$$

$$2\dot{C}OOH \longrightarrow (COOH)_2 \quad (oxalic \, acid), \tag{22a}$$
$$\longrightarrow HCOOH + CO_2, \tag{22b}$$

$$2HCO\dot{O} \rightarrow HCOOH + CO_2, \tag{23}$$

$$HCHO + R\cdot \rightarrow RH + \dot{C}HO, \tag{24}$$

$$2\dot{C}HO \longrightarrow (CHO)_2 \quad (glyoxal), \tag{25a}$$
$$\longrightarrow HCHO + CO, \tag{25b}$$

$$\dot{C}HO + \dot{C}H_2OH \rightarrow CHO.CH_2OH \tag{26}$$
$$(glycol \, aldehyde),$$

$$\dot{C}HO + \dot{C}OOH \rightarrow CHO.COOH \tag{27}$$
$$(glyoxylic \, acid),$$

$$\dot{C}H_2OH + \dot{C}OOH \rightarrow HOOC.CH_2OH \tag{28}$$
$$(glycolic \, acid).$$

It is to be mentioned that in the presence of air in methanol the formation of glycol, reaction (11b), was extremely reduced. By saturation of methanol with pure oxygen no glycol was detectable.

Conclusion

The radiation induced oxidation of methanol in the presence of air as well as in solutions containing different concentrations of pure oxygen (1 to 5 atm O_2) is leading to the formation of formic acid as a major final product in addition to other carboxylic acids. Depending on the content of oxygen in the solution the

G(acid)-values varied from 111.5 (air saturated samples) to 206 (5 atm O_2) indicating the existance of strong chain reactions. Formaldehyde is the second main product, followed by glycol aldehyde and oxalic acid. The other products (glyoxal, glyoxalic acid and glycolic acid) have very low yields ($G \leq 0.05$); therefore they were not taken further into account.

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