Radiolysis of Aqueous Ethanol in the Presence of CO

Hyoung-Ryun Park* and Nikola Getoff

Institut für Theoretische Chemie und Strahlenchemie der Universität Wien
und Ludwig-Boltzmann-Institut für Strahlenchemie und Strahlenbiologie, Währingerstraße 38,
A-1090 Wien, Austria

Z. Naturforsch. **47a**, 985–991 (1992); received June 29, 1992

First, the following rate constants (in $dm^3\ mol^{-1}\ s^{-1}$) were reported: $k(e_{aq}^- + C_2H_5OH) = (1.2 \pm 0.3) \times 10^3$, $k(H + C_2H_5OH) = (2.8 \pm 0.2) \times 10^7$ and $k(OH + C_2H_5OH) = (1.85 \pm 0.1) \times 10^9$.
The major radiolytic products resulting from aqueous 10^{-2}, 1 and 10 mol dm^{-3} ethanol were studied in the absence and presence of CO as a function of dose at pH 2 and 7. Probable reaction mechanisms are presented.

Introduction

The radiolysis of airfree as well as of oxygenated aqueous ethanol has been extensively studied in respect to various points of view, e.g. [1–3]. In deoxygenated aqueous solutions ($pH \geq 7$) the solvated electron (e_{aq}^-) is rather unreactive towards ethanol ($k \leq 400$ $dm^3\ mol^{-1}\ s^{-1}$ [4]). However, aqueous ethanol is attacked by H-atoms with $k = 1.3 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$ [5] and by OH-radicals with $k = 1.9 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ [6] in neutral and acidic solutions. The OH radicals withdrawn an H atom preferentially (85%) from the α-C-atom, 13% from C-2-position and 2% from the OH-group of the ethanol molecules [7]. In airfree solution, the CH_3CHOH species can dimerize to 2,3-butandiol or disproportionate to acetaldehyde and ethanol [3, 7].

In addition $G(H_2) = 4.05$ and hydrogen peroxide ($G = 0.6$) have been determined [8]. It has been also reported that in the presence of oxygen ($pH = 1.2$) the yield of hydrogen is strongly reduced up to $G(H_2) = 0.6$, and no 2,3-butandiol was found. However, the yield of H_2O_2 and acetaldehyde is increased, namely $G(H_2O_2) = 4.15$ and $G(CH_3CHO) = 2.6$, respectively [9]. Thereby the discovery of the rapid elimination of HO_2/O_2^- from α-hydroxylalkylperoxyl radicals brought a significant step for better understanding of the reaction mechanisms [10–12]. Finally, by means of pulse- and flash-conductometric measurements it was possible to elucidate the ethanol oxydation process and the formation of the final products (acetaldehyde, acetic acid, formic acid and peroxide) [13].

The aim of the present work was to investigate the radiation induced chemical behavior of the ethanol/CO system in aqueous solutions ($pH = 2$ and 7). Thereby ethanol concentrations of 10^{-2}, 1 and 10 mol dm^{-3} were used. In the last case the effect of direct radiolysis is also expected. The analyses were focussed mainly on the products resulting from the CO-participation in the chemical transformation of ethanol. In addition to the studies under steady-state conditions also some pulse radiolysis experiments were performed.

Experimental

Preparation of solutions. The solutions were prepared by using at least triply distilled water (quarz vessels) and p.A. chemicals (Merck). The aqueous ethanol solutions were first deoxygenated by purging high purity argon (30–40 min) and subsequently saturating with CO at room temperature (40 min, 10^{-3} mol dm^{-3} CO).

Irradiation source. A "Gammacell 220" served as ^{60}Co-γ-irradiation source (dose rate: 30 Gy min^{-1})* for steady-state experiments. Pulse radiolysis studies were also performed (0.4 μs pulses of 3 MeV electrons [14, 15].

Analysis. The formaldehyde yield was determined spectrophotometrically by means of the Hantz-method

---

* On leave from Department of Chemistry, Chonnam National University, Kwang-ju, 500-757, South Korea.

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

* 1 Gy = 100 rad = 1 Joule/kg = 1 Ws/kg.

0932-0784 / 92 / 0900-0985 $ 01.30/0. – Please order a reprint rather than making your own copy.

(described in [16]). The colored complex has $\varepsilon = 8000$ $dm^3\ mol^{-1}\ cm^{-1}$ at $\lambda = 412$ nm.

The yield of total aldehydes (formaldehyde, acetaldehyde and glyoxal) was measured using the method of Banks et al. [17]. Aliquot parts of the irradiated solutions were treated with 2,4-dinitrophenylhydrazine in order to convert the aldehydes into the corresponding hydrazones. The last ones were extracted with benzene, and the obtained extract was then treated by distillation under reduced pressure in order to remove the solvent. Subsequently the residue was disolved in dioxane and the aldehydes were separated by thin-layer chromatography (Silicagel plates, Merck) using toluene:benzene:$CCl_4 = 3:2:1$ as solvent (running time ca. 1 hour). The colored spots corresponding to formaldehyde ($R_f = 0.43$), acetaldehyde ($R_f = 0.42$) and glyoxal ($R_f = 0.22$) were individually extracted in 5 ml absolute ethanol, and after centrifugation of the solid phase the optical density for the determination of formaldehyde and acetaldehyde was measured at $\lambda = 350$ nm and for that of glyoxal at $\lambda = 430$ nm. The product yields were determined by means of calibration curves. The formaldehyde yield (determined by the Hantz-method) was substracted from the total aldehyde yield to obtain that of acetaldehyde. The glyoxalic acid was analyzed spectrophotometrically ($\lambda = 570$ nm, $\varepsilon = 1020$ $dm^3\ mol^{-1}\ cm^{-1}$ [18]).

The total yield of carboxylic acid was determined by titration with 5×10^{-3} mol dm^{-3} NaOH.

Results and Discussion

Pulse Radiolysis Experiments

Determination of $k(e^-_{aq} + C_2H_5OH)$ at pH = 9

The previously reported values of the rate constant for the reaction

$$e^-_{aq} + C_2H_5OH \rightarrow C_2H_5O^- + H \qquad (1)$$

are rather divergent, namely: $k_1(e^-_{aq} + C_2H_5OH) < 10^5\ dm^3\ mol^{-1}\ s^{-1}$ at pH = 12 [19], $k_1 = 1.1 \times 10^4\ dm^3\ mol^{-1}\ s^{-1}$ [20] and $k_1 \leq 400\ dm^3\ mol^{-1}\ s^{-1}$ [4].

This fact motivated us to undertake new measurements using a highly purified ethanol (distillation under argon and taking the middle fraction only), triple distilled water and p.A. $Ba(OH)_2$ for adjusting the pH of the solution. By applying 0.5 to 4 mol dm^{-3} aqueous ethanol and doses of 5–6 Gy per 0.4 µs pulse, the pseudo-first order decay of e^-_{aq} was followed at 720 nm.

After matrix-correction (solution without ethanol) using $k(e^-_{aq} + H_2O) = 16\ dm^3\ mol^{-1}\ s^{-1}$ [20], a rate constant, $k_1 = (1.2 \pm 0.3) \times 10^3\ dm^3\ mol^{-1}\ s^{-1}$ was obtained as a mean value of 10 determinations. This value does not agree with the two above ones. It might be mentioned that the rate constant for the e^-_{aq}-attack on both alcohols is reported by Hickel and Schmidt [4] to be the same. They have been performed by flash photolysis in basic solutions. No plausible explanation can be given for this discrepancy at present.

Determination of $k(H + C_2H_5OH)$ at pH = 2

This rate konstant has been previously determined by two groups: $k_2 = 1.3 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$ [5] and $k_2 = 2.1 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$ [21]. For completeness of our work we have also performed some pulse radiolysis experiments in this respect using 1×10^{-5} mol dm^{-3} MnO_4^- as a competitive reagent for H-atoms towards ethanol (10^{-2} to 5×10^{-2} mol dm^{-3}) in airfree solutions (pH = 2) [22],

$$C_2H_5OH + H \longrightarrow \dot{C}_2H_4OH + H_2, \qquad (2)$$
$$(k_2 \text{ to be determined})$$

$$MnO_4^- + H \longrightarrow MnO_4^{2-} + H^+, \qquad (3)$$
$$k_3 = 2.36 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}\ [22].$$

Applying low doses (~5 Gy/0.4 µs pulse), the change of the MnO_4^- absorption was followed at $\lambda = 545$ nm. Several determinations resulted in $k_2 = (2.8 \pm 0.2) \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$, which is in very good agreement with the previous published data.

Determination of $k(OH + C_2H_5OH)$ at pH = 9

There are a number of studies done in this respect ranging from pH 1 to 11 with k-values from 1.6×10^9 to $2.2 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ [23]. The selected value is $k = 1.9 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$. In the present work this subject matter was reinvestigated using 2.5 to 5×10^{-5} mol dm^{-3} ferrocyanide as competitive reagent in 5×10^{-4} mol dm^{-3} ethanol saturated with N_2O (2.8×10^{-2} mol dm^{-3} at pH = 9),

$$C_2H_5OH + OH \longrightarrow \dot{C}_2H_4OH + H_2O, \qquad (4)$$
$$(k_4 \text{ to be determined})$$

$$Fe(CN)_6^{4-} + OH \longrightarrow Fe(CN)_6^{3-} + OH^-, \qquad (5)$$
$$k_5 = 1 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}\ [24].$$

The pseudo-first order kinetics of the ferrocyanide absorption change at 420 nm serviced as basis for the calculation of the k_4-value. The mean value of several measurements was $k_4 = (1.85 \pm 0.1) \times 10^9$ dm^3 mol^{-1} s^{-1} which is rather similar to the above mentioned selected value.

Steady-state Radiolysis and Product Analysis

The formation of the final products is a result of the competition reactions of the primary species of water radiolysis (e^-_{aq}, H, and OH) with both substrates, CO and ethanol. The dose dependence of the major radiolytic products resulting from a 10^{-2} mol dm^{-3} $C_2H_5OH/10^{-3}$ mol dm^{-3} CO system at pH 2 and 7 is presented in Figure 1.

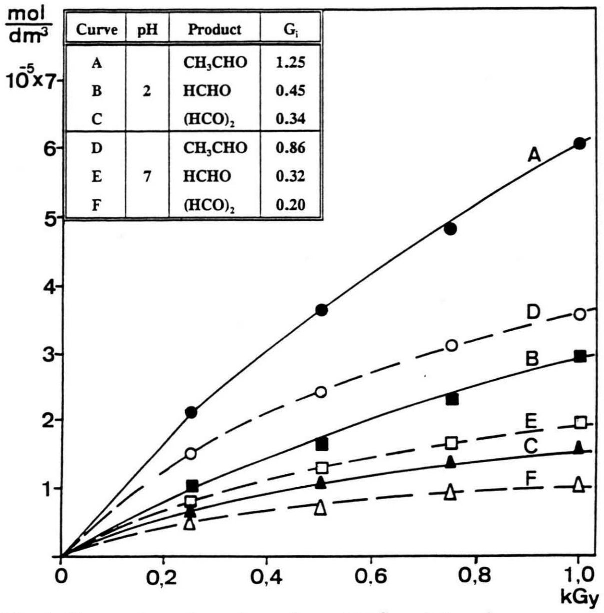


Fig. 1. Formation of products from 10^{-2} mol dm^{-3} aqueous ethanol saturated with CO at pH 2 and 7 as a function of dose. Insert: initial G-values (G_i) of the major products.

The yields of acetaldehyde, formaldehyde and glyoxal are essentially higher at pH 2 compared to those observed at pH 7 (Fig. 1 insert). A similar effect has previously been observed for aqueous methanol/CO system [25]. The yield-dose curves are tending to a saturation, indicating the occurrence of a product radiolysis at doses higher than 0.3 kGy.

The formation reaction of the main products in acid solution (pH = 2) can be summed up as follows:

$$e^-_{aq} + H^+_{aq} \longrightarrow H \qquad (6)$$

$k_6 = 2.3 \times 10^{10}$ dm^3 mol^{-1} s^{-1} [19],

$$CO + H \longrightarrow H\dot{C}O \qquad (7)$$

$k_7 = 3.8 \times 10^8$ dm^3 mol^{-1} s^{-1} [26],

$$2\,H\dot{C}O \longrightarrow CO + HCHO \text{ (formaldehyde)} \qquad (8a)$$

$$\phantom{2\,H\dot{C}O} \longrightarrow (CHO)_2 \text{ (glyoxal)} \qquad (8b)$$

$$CO + OH \longrightarrow \dot{C}OOH \qquad (9)$$

$k_9 = 8.3 \times 10^8$ dm^3 mol^{-1} s^{-1} [27],

$$\dot{C}OOH \rightleftharpoons \dot{C}O_2^- + H^+ \qquad (10)$$

pK = 1.4 [28],

$$2\dot{C}OOH \longrightarrow CO_2 + HCOOH \qquad (11a)$$

$$\phantom{2\dot{C}OOH} \longrightarrow (COOH)_2, \qquad (11b)$$

$$\dot{C}OOH + H\dot{C}O \rightarrow HCOO.CHO, \qquad (12)$$

$$2\,\dot{C}O_2^- \longrightarrow (CO_2^-)_2 \text{ (oxalate)}, \qquad (13)$$

$k_{13} = 1.26 \times 10^9$ dm^3 mol^{-1} s^{-1} [29].

Only traces of formic acid as well as oxalic and glyoxalic acid could be found, indicating that reactions (9) to (13) can be neglected. In diluted aqueous ethanol (10^{-2} mol dm^{-3}) in the presence of CO (10^{-3} mol dm^{-3}) 96% of the OH radicals and ca. 50% of the H atoms are leading mainly to the formation of the $CH_3\dot{C}HOH$ radicals, reactions (2) and (4). The resulting species can undergo several reactions:

$$2\,CH_3\dot{C}HOH \longrightarrow CH_3CH_2OH + CH_3CHO \qquad (14a)$$

(acetaldehyde, $G = 1.25$),

$$\phantom{2\,CH_3\dot{C}HOH} \longrightarrow CH_3CH(OH)CH(OH)CH_3$$

(2,3-butandiol, $G = 0.6$), (14b)

$$CH_3\dot{C}HOH + H\dot{C}O \rightarrow CH_3CH(OH)CHO \qquad (15)$$

(α-hydroxypropionic aldehyde, $G = 0.6$).

Some experiments in basic solutions of 10^{-2} mol · dm^{-3} ethanol and 10^{-3} mol dm^{-3} CO system showed the previously observed formation of formate [26, 27, 30, 31]:

$$CO + e^-_{aq} \longrightarrow CO^-_{aq} \qquad (16)$$

($k_{16} = 1 \times 10^9$ dm^3 mol^{-1} s^{-1} [26]).

CO^-_{aq} is identical with the $HCOOH^-$ species which can give rise of a chain reaction:

$$HCOOH^- + OH^-_{aq} \longrightarrow HCOO^- + e^-_{aq}, \qquad (17)$$

$$HCOO^- + OH \longrightarrow \dot{C}O_2^- + H_2O \qquad (18)$$

($k_{18} = 2.5 \times 10^9$ dm^3 mol^{-1} s^{-1} [32]),

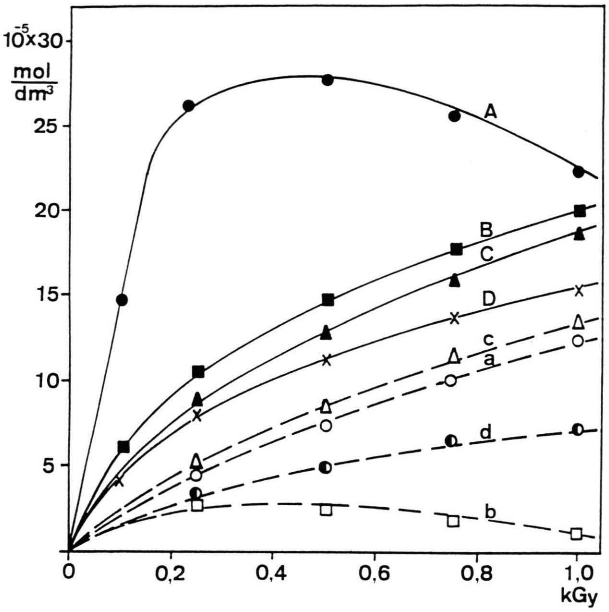


Fig. 2. Formation of acetaldehyde from aqueous ethanol as a function of dose. *I. Series:* 1 mol dm^{-3} ethanol airfree, (a) pH 2, (b) pH 7; saturated with CO, (c) pH 2 and (d) pH 7. *II. Series:* 10 mol dm^{-3} ethanol airfree, (A) pH 2, (B) pH 7; saturated with CO, (C) pH 2 and (D) pH 7.

Table 1. Formation of acetaldehyde from 1 and 10 mol dm^{-3} aqueous ethanol at pH 2 and 7 in the absences and presence of CO.

C_2H_5OH [mol dm^{-3}]	Curve Nr. in Fig. 2	pH	CO [mol dm^{-3}]	G_i
1	a	2	–	2.0
	b	7	–	1.8
	c	2	10^{-3}	2.8
	d	7	10^{-3}	1.9
10	A	2	–	15.4
	B	7	–	12.8
	C	2	10^{-3}	5.7
	D	7	10^{-3}	5.5

$$CH_3\dot{C}HOH + \dot{C}O_2^- \longrightarrow CH_3CH(OH)COO^- \quad (19)$$
(α-hydroxypropionate ion).

This reaction pathway was not further studied.

The formation of acetaldehyde in 1 mol dm^{-3} as well as 10 mol dm^{-3} ethanol in the absence and presence of CO at pH 2 and 7 was investigated as a function of dose. The results are presented in Figure 2.

In the first series of experiments: airfree 1 mol dm^{-3} ethanol it is obvious that the acetaldehyde yield at pH 2 (curve a) is much higher than that at pH 7 (curve b in Figure 2). The same pH-effect is observed in the ethanol solutions containing CO (compare curves c and d in Figure 2).

In the case of 10 mol dm^{-3} ethanol (second series in Fig. 2) the highest yield of acetaldehyde was obtained in airfree solution at pH 2, followed by that at pH 7 (curves A and B in Figure 2). In the presence of CO the yields at pH 2 and 7 are even lower. The G_i-values of acetaldehyde of both series in absence and presence of CO are calculated and presented in Table 1. In the first case the presence of CO is contributing to the formation of acetaldehyde (compare e.g. the G-values at pH 2 in absence and presence of CO). Based on this fact it is obvious that direct radiolysis of alcohol is involved in the process, in course of which C–C bond cleavage takes place leading to the formation of $\dot{C}H_3$ and $\dot{C}H_2OH$ radicals among H-atoms, $\dot{C}H_2OH$ and other species [3]. Hence in airfree ethanol solution reactions (14a) and (14b) in addition to reactions (20a) and (20b) are playing an important role:

$$2\,\dot{C}H_2OH \longrightarrow CH_3OH + HCHO \quad (20a)$$
$$\longrightarrow (CH_2OH)_2 \quad (20b)$$
$$k_{20} = 2.8 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}\ [33].$$

In solution saturated with CO, reaction (7) is also involved and the resulting $H\dot{C}O$ radicals can combine with $\dot{C}H_3$ and $\dot{C}H_2OH$ species in competition to reactions (8a) and (8b):

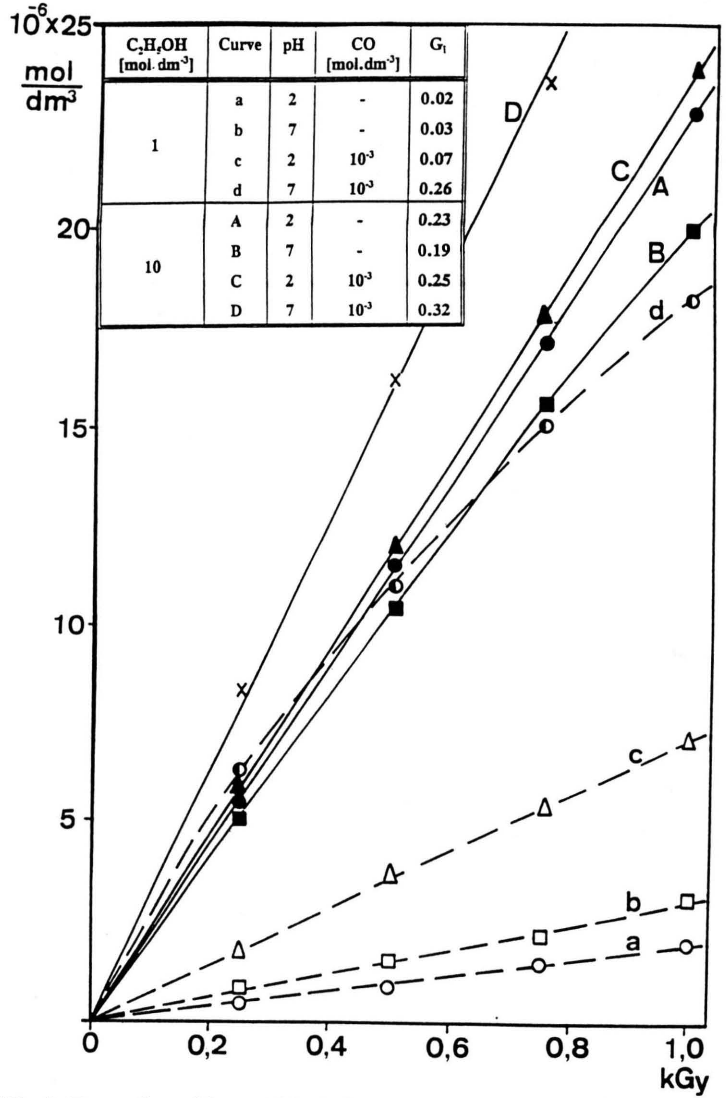
$$\dot{C}H_3 + H\dot{C}O \longrightarrow CH_3CHO \quad (21)$$
$$\dot{C}H_2OH + H\dot{C}O \longrightarrow CH_2(OH)CHO \quad (22)$$
(glycolaldehyde).

Only traces of glycolaldehyde were detected, but its yield was not determined.

Using 10 mol dm^{-3} ethanol in deoxygenated solutions, the yield of acetaldehyde is strongly increased, $G = 15.4$ at pH 2 and $G = 12.8$ at pH 7, respectively, being observed. This fact can be explained by the reaction of various transients (R), e.g. H, $\dot{C}H_3$, $\dot{C}H_2OH$ etc. with ethanol in addition to H, OH leading finally to resulting in $CH_3\dot{C}HOH$ species, (23). The last ones are disappearing by reactions (14a) and (14b),

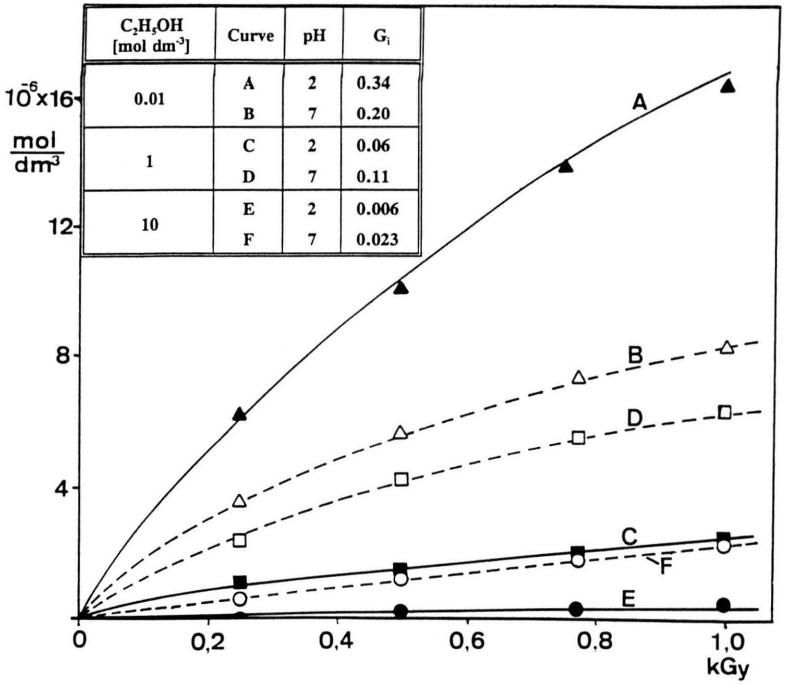
$$CH_3CH_2OH + \dot{R} \longrightarrow CH_3\dot{C}HOH\,. \quad (23)$$

In aqueous 10 mol dm^{-3} ethanol saturated with CO the yield of acetaldehyde is strongly decreased in comparison to the airfree solutions (Fig. 2, Table 1).



C_2H_5OH [mol·dm^{-3}]	Curve	pH	CO [mol.dm^{-3}]	G_i
1	a	2	-	0.02
	b	7	-	0.03
	c	2	10^{-3}	0.07
	d	7	10^{-3}	0.26
10	A	2	-	0.23
	B	7	-	0.19
	C	2	10^{-3}	0.25
	D	7	10^{-3}	0.32

Fig. 3. Formation of formaldehyde from aqueous ethanol as a function of dose. *I. Series:* 1 mol dm^{-3} ethanol airfree, (a) pH 2, (b) pH 7; saturated with CO, (c) pH 2 and (d) pH 7. *II. Series:* 10 mol dm^{-3} ethanol airfree, (A) pH 2, (B) pH 7; saturated with CO, (C) pH 2 and (D) pH 7. Insert: calculated G_i-values.



C_2H_5OH [mol dm^{-3}]	Curve	pH	G_i
0.01	A	2	0.34
	B	7	0.20
1	C	2	0.06
	D	7	0.11
10	E	2	0.006
	F	7	0.023

Fig. 4. Formation of glyoxal as a function of dose using 0.01, 1 and 10 mol dm^{-3} aqueous ethanol saturated with CO at pH 2 and 7. Insert: calculated G_i-values.

This observation can be explained by the fact that CO is consuming part of the H-atoms resulting in $H\dot{C}O$ radicals, reaction (7), which can give rise in the formation of formaldehyde, reaction (8a) and glyoxal, reaction (8b). The yields of formaldehyde using 1 and 10 mol dm^{-3} ethanol in absence and presence of CO are presented in Fig. 3 as function of dose.

They are about one order of magnitude lower than those of acetaldehyde obtained under more similar experimental conditions. It is remarkable that in this the G(HCHO)-values at pH 2 are lower than those obtained at pH 7, which is in contradiction with the results observed in 10^{-2} mol dm^{-3} ethanol (see Table in Figure 1).

The same pH-effect is also observed for the glyoxal yields resulting from 10^{-2}, 1 and 10 mol dm^{-3} ethanol in the presence of 10^{-3} mol dm^{-3} CO at pH 2 and 7 (Fig. 4), namely, in diluted aqueous ethanol at pH 2 the yield of glyoxal is essentially higher than that at pH 7. But, using 1 or 10 mol dm^{-3} ethanol the pH influence is just opposite: the yields in neutral solutions are higher. Also, with increasing the ethanol concentration the glyoxal yield is strongly reduced. This effect is explainable by the following fact: With increasing ethanol concentration the formation of H-atoms is facilitated as a consequence of the direct radiolysis effect. However, the H-atoms are preferentially scavanged by the ethanol and reaction (7) (formation of $H\dot{C}O$ radicals) is suppressed. Hence, mainly the yield of $CH_3\dot{C}HOH$ is essentially increased, see reaction (23), resulting in acetaldehyde and 2,3-butandiol.

Conclusion

The rate constants of the reactions of e^-_{aq}, H-atoms and OH radicals with aqueous ethanol were redetermined (see Abstract).

The formation of the major products resulting from steady state radiolysis of aqueous 10^{-2} to 10 mol dm^{-3} ethanol in the absence and presence of CO at pH 2 and 7 was studied. Using 10^{-2} mol dm^{-3} ethanol, the yields of the final products are depending on the primary products of water radiolysis (OH, H, and e^-_{aq}). Their yields are higher in acid solutions than those in neutral media. In concentrated ethanol solutions (1 and 10 mol dm^{-3}) in the absence and presence of CO the effect of the direct radiolysis of substrate is playing an essential role. In this case the formation mainly of the $CH_3\dot{C}HOH$ radicals is favoured, whereas the yield of $H\dot{C}O$ is suppressed. Hence, the distribution of the final products, studied as a function of dose, is different compared to that in diluted solution.

Acknowledgement

One of us (H. R. Park) thanks the Federal Ministry for Science and Research in Austria for the financial support of a postdoctoral fellowship.

[1] L. Kevan, Actions Chimiques et Biologiques des Radiations (M. Haissinsky, ed.), ser. 13, p. 57. Masson et Cie., Paris 1969.

[2] G. R. Freeman, Actions Chimiques et Biologiques des Radiations (M. Haissinsky, ed.), ser. 14, p. 73. Masson et Cie., Paris 1969.

[3] J. W. T. Spinks and R. J. Woods, Introduction to Radiation Chemistry, 3rd ed., J. Wiley & Sons Inc., New York 1990.

[4] B. Hickel and K. H. Schmidt, J. Phys. Chem. **74,** 2470 (1970).

[5] B. Smaller, E. C. Avery, and J. R. Remko, J. Chem. Phys. **55,** 2414 (1971).

[6] B. S. Wolfenden and R. L. Willson, J. Chem. Soc. Perkin Trans. II, 805 (1982).

[7] K. D. Asmus, H. Möckel, and A. Henglein, J. Phys. Chem. **77,** 1218 (1973).

[8] J. T. Allan, E. M. Hayon, and J. Weiss, J. Chem. Soc. London **1959,** 3913.

[9] G. G. Jayson, G. Scholes, and J. Weiss, J. Chem. Soc. London **1957,** 1358.

[10] Y. Han, J. Rabani, and A. Henglein, J. Phys. Chem. **80,** 1558 (1976).

[11] E. Bothe, D. Schulte-Frohlinde, and C. von Sonntag, J. Chem. Soc., Perkin Trans. II, 416 (1978).

[12] E. Bothe, M. N. Schuchmann, D. Schulte-Frohlinde, and C. von Sonntag, Photochem. Photobiol. **28,** 639 (1978).

[13] E. Bothe, M. N. Schuchmann, D. Schulte-Frohlinde, and C. von Sonntag, Z. Naturforsch. **38b,** 212 (1983).

[14] N. Getoff and F. Schwörer, Radiat. Res. **41,** 1 (1970).

[15] N. Getoff, A. Ritter, and F. Schwörer, Radiat. Phys. Chem. **28,** 343 (1986).

[16] T. Nash, Biochem. J. **55,** 418 (1958).

[17] T. Banks, C. Vaughn, and L. M. Marshalle, Analyt. Chem. **27,** 1348 (1955).

[18] M. Pesez and J. Bartos, Bull. Soc. Chim. France, 481 (1960).

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

[20] M. Anbar and P. Neta, Int. J. Appl. Radiat. Isotop. **18,** 493 (1967).

[21] R. W. Fessenden and N. C. Verma, Faraday Disc. Chem. Soc. **63,** 104 (1977).
[22] J. H. Baxendale, J. P. Keene, and D. A. Stoff, Pulse Radiolysis (M. Ebert, J. P. Keene, A. J. Swallow, and J. H. Baxendale, eds.), Academic Press, London 1965, p. 107.
[23] Farhataziz and A. B. Ross, Selected Specific Rates of Reactions of Transients from Water in Aqueous Solution III. Hydroxyl Radical and Perhydroxyl Radical and Their Radical Ions. Nat. Bur. of Standards, Washington 1977.
[24] A. J. Elliot and A. S. Simsons, Radiat. Phys. Chem. **24,** 229 (1984).
[25] N. Getoff and D. Seitner, Z. Phys. Chem. N.F. **51,** 27 (1966).
[26] N. Getoff and H. P. Lehmann, Int. J. Radiat. Phys. Chem. **2 (2),** 91 (1970).
[27] Y. Raef, J. K. Thomas, and S. Gordon, Radiation Res. Suppl. **4,** 74 (1964).
[28] G. V. Buxton and R. M. Sellers, J. C. S. Faraday Trans. I, **69,** 555 (1973).
[29] N. Getoff, Intern. J. Energy Environm. economics, in print.
[30] D. Seitner and N. Getoff, Z. Phys. Chem. **66,** 22 (1969).
[31] H. R. Park and N. Getoff, Z. Naturforsch. **43a,** 430 (1988).
[32] J. K. Thomas, Faraday Soc. **61,** 702 (1965).
[33] N. Getoff, A. Ritter, and F. Schwörer, J. C. S. Faraday Trans. I, **79,** 2389 (1983).