

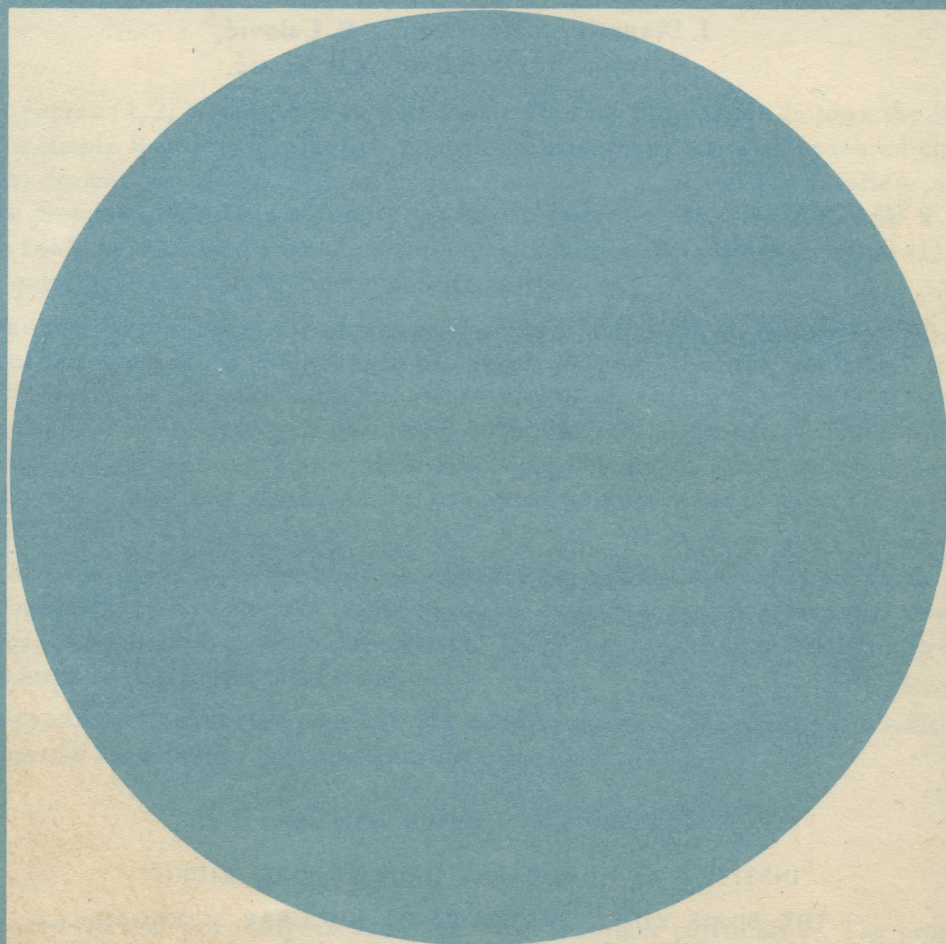
BULLETIN
OF THE BORIS KIDRIČ INSTITUTE
OF NUCLEAR SCIENCES

Vol. 19
Chemistry, No. 2

RADIOLYTIC PRODUCTS IN AQUEOUS
OXALIC ACID DOSIMETER

by

Vitomir Marković and Bohumil Bartoniček,
Department of Radiation Chemistry



VINČA
Yugoslavia
1968

Editor: I. DRAGANIĆ

Editorial Board:

I. Draganić, S. Hajduković, B. Lalović,
M. Vojinović, N. Raišić, M.M. Ristić

INSTITUT ZA NUKLEARNE NAUKE "BORIS KIDRIČ"
THE BORIS KIDRIČ INSTITUTE OF NUCLEAR SCIENCES
BEOGRAD, P.O. BOX 522

Štampano u Institutu za nuklearne nauke "Boris Kidrič", Vinča
Tiraž 500

RADIOLYTIC PRODUCTS IN AQUEOUS OXALIC ACID DOSIMETER

by

*Vitomir Marković and Bohumil Bartoniček**, Department of Radiation Chemistry

Initial yields and complete dosage curves were obtained for carbon dioxide, hydrogen, formaldehyde, glyoxal and hydrogen peroxide. Following compounds were not found among radiolytic products: carbon monoxide, glyoxylic acid, mesoxalic acid, glycolic and formic acid. There is an evidence for 75% C atoms among measured products. The complete material balance has not been obtained. Postreactions of some products (hydrogen peroxide, glyoxal) indicate the presence of some chemical reactions, which can occur simultaneously with the radiation chemical reactions.

I n t r o d u c t i o n

Recent papers (1, 2, 3) have shown that oxalic acid decomposition follows the first order kinetics and a simple logarithmic equation relates the absorbed dose and measured chemical effect. However, comparison of the calibration data obtained in different laboratories shown that values for the proportionality factor in the logarithmic equation are obtained with a dispersion larger than it could be expected from the accuracy of decomposition measurements (1). In all cases the first order kinetics was confirmed satisfactorily.

The reaction mechanism in the presence of oxygen is fairly well understood (4). Much less is known about the reactions in the absence of oxygen and in dosimetric, noninitial conditions. In the absence of oxygen Draganić obtained initial yields of carbon dioxide 7.8, formaldehyde 0.08 and glyoxal 0.004 (5). Hydrogen was found in the molecular yield 0.46. Other products such as carbon monoxide, glyoxylic and mesoxalic acid were not found. Sehested *et al.* (6) proved the presence of glyoxylic acid and glyoxal in the irradiated solutions and showed the existence of some post-effect.

It was obvious that much more work was needed on radiolytic product yields in dosimetric conditions, especially of those products which could, even at low concentrations, compete efficiently with oxalic acid for free radicals in water. Therefore, we tried to identify the oxalic acid radiolytic products in dosimetric conditions.

In all experiments, whenever possible, we tried to maintain the identical conditions with those of dosimetric experiments performed earlier (1).

E x p e r i m e n t a l d e t a i l s

Solutions

Oxalic acid (Merck) pro analysis was used without further purification. The preparation of the solution and cleaning of the vessels was the same as in the preceding work (1). Pyrex am-

* Institute of Nuclear Research, Řež near Prague, Czechoslovakia.

poules with ground glass caps were mostly used, except for gas measurements in which sealed ampoules were used and solutions degassed by standard techniques. All other chemicals were BDH products.

Irradiation and dosimetry

Samples were irradiated in the laboratory 3.5 kCi ^{60}Co source at an absorbed dose rate of approximately 8.10^{19} eV ml^{-1} per hour. The absorbed dose rate was determined with the Fricke dosimeter ($k = 2197 \text{ M}^{-1} \text{ cm}^{-1}$ at 25°C and $G(\text{Fe}^{3+}) = 15.6$).

Gas analysis

Two methods for the determination of gases in irradiated solutions were used. Small quantities of carbon dioxide (below 100 mm^3) and hydrogen were determined by gas chromatography, and for larger quantities of carbon dioxide the Van Slyke apparatus was used. For the identification of carbon monoxide the gas chromatographic method was used.

Paper chromatography

Paper chromatography was employed for the qualitative determination of products containing a carbonyl group. Standard methods of analysis were applied (7): 2,4-dinitrophenylhydrazine solution in 1:1 hydrochloric acid was added to the irradiated solutions. The hydrazons were extracted by chloroform and analyzed by paper chromatography on Whatman No. 1 paper ($40 \times 2.5 \text{ cm}$). Butanol saturated with 3% ammonia served as a mobile phase.

The products were identified by determining the R_f - values in the developed chromatogram, by the colour of the spots after spraying with 10% potassium hydroxide and by measuring the absorption spectra in the visible and UV light region. For the last determination, a strip of paper was cut in sections, hydrazon extracted with methanol and 10% potassium hydroxide in methanol added (8).

Spectrophotometric methods

The different organic products and hydrogen peroxide as well, were determined by the spectrophotometric methods of analysis. These methods are not selective enough and to determine formaldehyde and glyoxal, several methods were used simultaneously. Technical details of the methods are presented in Table I.

Table I
Details for the spectrophotometric methods

Reagent	Compound measured	Maximum of absorption $\text{m}\mu$	Molar ext. coefficient $\text{M}^{-1} \text{ cm}^{-1}$	Validity of Lambert-Beer's law, μM	Ref.
2,7 Dihydroxynaphthalene	Formaldehyde	540	22 000 ^a	5-30	9
	Glyoxal	540	10 500 ^a	10-100	
Phenylhydrazine hydrochloride (alkaline media)	Formaldehyde	510	24 400	4-13	,
	Glyoxal	510	1 500 ^a	-	
Phenylhydrazine hydrochloride (acid medium)	Formaldehyde	520	8 750	-	10
	Glyoxal	420	34 800	-	
Resorcin	Glyoxylic acid	560	9 000 16 000 ^a	5-60	9
Potassium iodide	Hydrogen peroxide	355	25 000	-	11

a) reported by Lj. Josimović et al. (9)

Lambert-Beer's law does not hold for the 2,7-dihydroxynaphthalene method for very low concentrations of formaldehyde (below $1.6 \mu\text{M}$). The formaldehyde concentration was read directly from the non-linear calibration curve. The determination error was not higher than $\pm 5\%$.

The phenylhydrazine method in alkaline medium differed from the reported one (9), as the aliquots of irradiated solutions were not neutralized. The molar extinction coefficient was dependent on the batch of the reagent used. The reproducibility of this method was rather low and the error of determination was about $\pm 10\%$. This was probably due to the variations in the time interval between the addition of the reagents and the measurement. By using the method with phenylhydrazine in acidic medium, the maximum for glyoxal was obtained at $420 \text{ m}\mu$ instead of $355 \text{ m}\mu$, as given in the literature (10). The standard solutions of glyoxal, in the presence of oxalic acid, have a stable maximum for several days.

Results

Identifications

Organic products in the irradiated solutions were identified by paper chromatography. The presence of formaldehyde and glyoxal was confirmed on the basis of the R_f values and the absorption spectra of potassium hydrazone salts. Likewise, the characteristic maximum for formaldehyde ($520 \text{ m}\mu$) and glyoxal ($420 \text{ m}\mu$) was found in the irradiated solutions after reaction with phenylhydrazine in acidic medium (10).

A significant amount of CO could not be found and $G(\text{CO})$ must be lower than 0.01. The paper chromatography test for the glyoxylic and mesoxalic acids as well as the test for glyoxylic acid with resorcin (9) were negative. A post effect was observed during analyses with phenylhydrazine in acidic medium. When measurements were performed immediately after irradiation (not later than 15 minutes) maximum absorption, characteristic for glyoxal, appeared. However, one day later the maximum was shifted from 420 to $365 \text{ m}\mu$. A similar effect was observed when H_2O_2 was added to the unirradiated glyoxal in oxalic acid solution.

The yield determinations

The results of quantitative measurements of different products are given in Fig. 1. The range of absorbed doses was chosen so as to follow the oxalic acid decomposition in the range up to about 50%. The solid line in the upper part of the diagram shows the number of oxalic acid molecules decomposed. This curve is calculated from the logarithmic equation for the oxalic acid dosimeter (1).

Figure 2 presents results given as the ratio of the CO_2 molecules formed to the oxalic acid molecules decomposed as a function of the percentage of decomposition. The determination was performed in three different initial concentrations (50, 250 and 500 mM). No significant difference between the different initial concentrations was observed. The ratio of the G values is

$$\frac{G(\text{CO}_2)}{G(-\text{H}_2\text{C}_2\text{O}_4)} = 1.42 \pm 0.05$$

Careful measurements were performed to determine the initial yields of the products. For this purpose deaerated solutions were used. The results of determination are given in Table II.

The $(\text{CHO})_2$, HCHO and H_2O_2 yields decreased with increasing absorbed dose. Measured G-values were plotted against the absorbed doses and extrapolated to zero absorbed dose in order to obtain initial yields. The CO_2 yield was constant up to about $1.9 \cdot 10^{19} \text{ eV}\cdot\text{ml}^{-1}$.

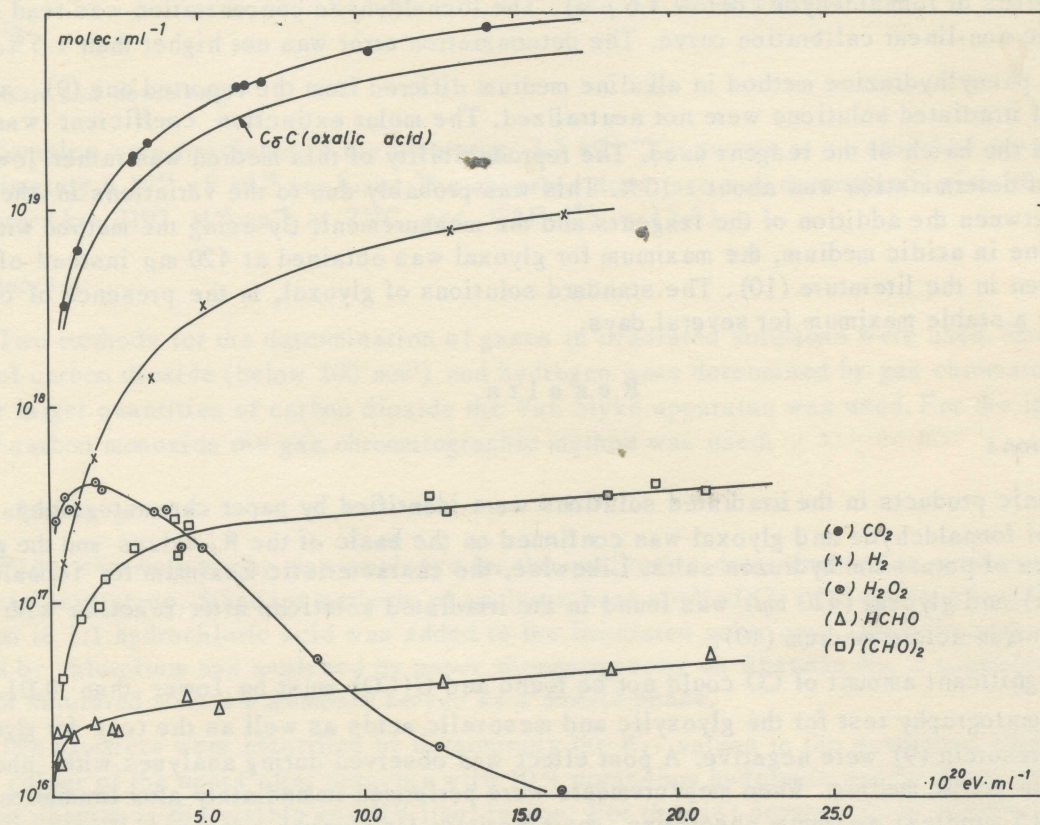


Fig. 1. - The accumulation of different products in aqueous oxalic acid dosimeter; ^{60}Co gamma radiation; initial concentration 250 mM; natural pH of the solution

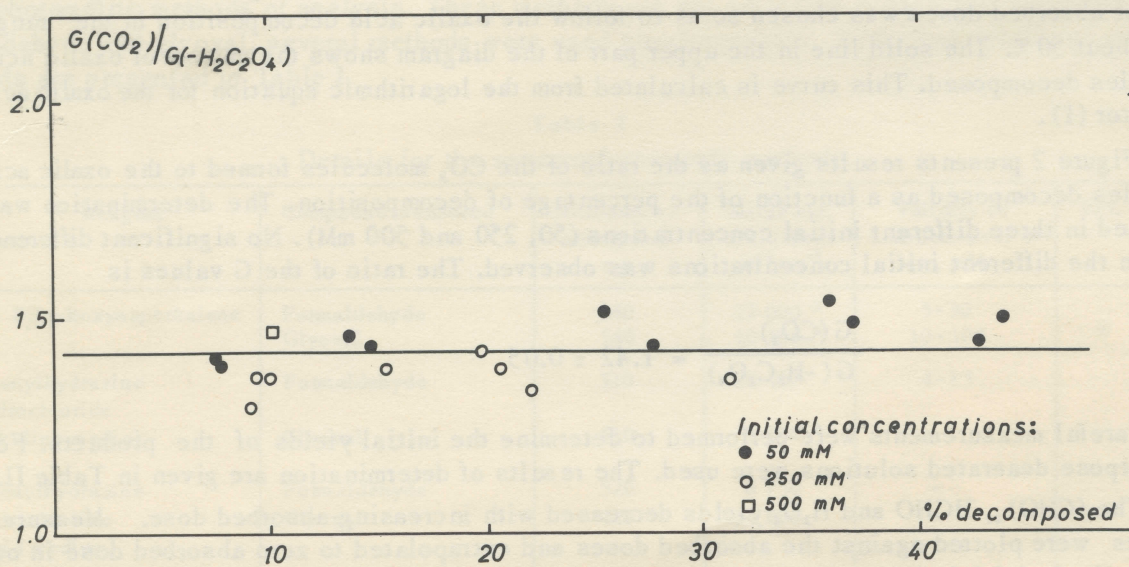


Fig. 2. - The ratio of yields for CO_2 formation and oxalic acid decomposition

Table II

Initial yields of radiolytic products	
Product	G_{initial}
CO ₂	8.43
H ₂	0.4
HCHO	0.2
(CHO) ₂	0.1
H ₂ O ₂	0.73
CO ₂ ^a	5.70
H ₂ O ₂ ^a	3.89

a — in presence of oxygen

Discussion

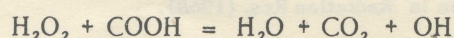
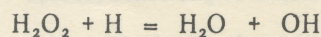
The accumulation of different products (Fig. 1) and their initial yields (Table II) explain some reactions occurring in the aqueous oxalic acid dosimeter. They will be discussed separately for different products.

Carbon dioxide. Assuming that each reducing radical in irradiated water (H atom or e_{aq}^-) gives rise to one CO₂ molecule and each OH radical to two CO₂ molecules (5), the theoretical ratio between the number of CO₂ molecules formed and the oxalic acid molecules decomposed should be 1.45. This value is in good agreement with the experimental 1.42 ± 0.05 in a wide range of decompositions and concentrations. The constant value of this ratio and the shape of the CO₂ curve vs. absorbed dose indicate that CO₂ is the primary and stable product of oxalic acid radiolysis. The determination of $G(\text{CO}_2)$ in the presence of oxygen gave a value in good agreement with the one determined earlier (4).

Hydrogen. In initial conditions and in concentrated solutions the measured yield of hydrogen corresponds to G_{H_2} . At higher absorbed doses, close to $5 \cdot 10^{20}$ eV.ml⁻¹, where appreciable amounts of glyoxal and formaldehyde are formed, an increase in the total yield up to 0.7 and then a continuous and slow decrease were observed. This can be ascribed to the reactions of glyoxal or some other products with H atoms.

Formaldehyde and glyoxal. These products are formed, most probably, in different reactions of organic radicals formed by oxalic acid reactions with H and OH radicals (5). The shape of the dosage curves indicated that these products are the primary products of oxalic acid radiolysis which are not stable and undergo further reactions through which they disappear. These reactions could be chemical (like polymerization) or radiation chemical (competitive reactions with oxalic acid for H and OH radicals).

Hydrogen peroxide. In the absence of oxygen, the measured yield of hydrogen peroxide corresponds to $G_{\text{H}_2\text{O}_2}$. The measured value 0.73 is in good agreement with 0.7 to 0.8 given for the acidic medium by different authors (12). In the dosimetric conditions with oxygen initially present, hydrogen peroxide is formed with the yield 3.8 until all oxygen in the solution is consumed (at about 5 to $6 \cdot 10^{18}$ eV.ml⁻¹). Thereafter the concentration continuously decreases. It can be ascribed to the reactions (12)



which occur even at very low concentrations of hydrogen peroxide in the absence of oxygen.

Oxalic acid decomposition. It is the result of reactions with the primary radiolytic products of water, i.e. with the reducing and oxidizing radicals. In initial conditions, the yield should be equal to the sum of radical yields, i.e.

$$G_o(-\text{H}_2\text{C}_2\text{O}_4) = G_{\text{red}} + G_{\text{OH}} = 6.4$$

This value, however, cannot be measured directly. It can only be calculated from the initial CO_2 yield and the theoretical ratio between these two yields (confirmed for non-initial conditions):

$$G_o(-\text{H}_2\text{C}_2\text{O}_4) = \frac{8.43}{1.45} = 5.8^*$$

This value is about 10% lower than the one calculated from accepted values for radical yields (12). The difference can be explained if some back reactions take place. It was shown (13) that recombination of COOH radicals into oxalic acid does not occur, but other reactions are not excluded. Besides, very fast reactions of oxalic acid with e_{aq}^- (14) may not always result in oxalic acid decomposition, as was proved in the presence of oxygen (15). Finally, with a

$$k_{\text{H} + \text{H}_2\text{C}_2\text{O}_4} < 10^6 \text{ M}^{-1} \text{ sec}^{-1} \quad (14),$$

the oxalic acid concentration is not sufficient to scavenge all H atoms. It is difficult to estimate which of these effects is the most important. It is but sure that the last one does not exceed a few percents.

The product yields give evidence in 75% of C atoms of the decomposed oxalic acid molecules. The absence of other simple compounds indicates that some more complicated products are also formed. They are most probably aldehyde-type compounds or polymers of formaldehyde and glyoxal.

The initial yields of all products are higher than those measured earlier (5), especially of formaldehyde and glyoxal. These results as well, do not give material balance but they can be useful in explaining the first order decomposition of oxalic acid (16).

In non-initial conditions the presence of radiolytic products affect the course of the dosage curve for oxalic acid. The oxalic acid decomposition yield decreases with increasing absorbed dose. Some preliminary-experiments (16) showed that formaldehyde and glyoxal in competition with oxalic acid for H and OH radicals, can be responsible for the apparent first order decomposition of oxalic acid. Different concentrations of these products in dosimetric solution would then affect the calibration factor.

A c k n o w l e d g e m e n t s

The authors wish to express their gratitude to Dr. I. Draganić for may valuable discussions and suggestions during this work. Thanks are also due to Mr. N. Stančić for technical assistance.

R E F E R E N C E S:

1. Marković, V. and I. Draganić, New Possibilities for Routine Use of Oxalic Acid Solutions in Multimegarad Gamma Radiation Dosimetry, *Radiation Res.*, to be published (1968).
2. Marković, V. and I. Draganić, New Possibilities for Routine Use of Oxalic Acid Solutions in In-Pile Dosimetry, submitted for publication in *Radiation Res.* (1968).
3. Holm, N.W., E. Bjergbakke, K. Sehested and I. Draganić, Risø Report No. 111 (1967).

* The extrapolation of decomposition yields, measured above 15% of decomposition, to zero absorbed dose gives 5.6 for the initial yield, but the former value was assumed to be more reliable.