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EFFECTS OF RADIATION ON AQUEOUS SOLUTIONS OF CARBOXYLIC ACIDS

By R. A. Penneman

ABSTRACT

Irradiation of aqueous solutions of oxalic acid, $(\text{COOH})_2$, with 2.5 Mev x rays for exposure of $\sim 10^6$ roentgens causes a decrease in the number of both reducing and acid equivalents. Solutions of formic acid, HCOOH , show similar decreases under deuteron and electron irradiation. Approximate values of G (molecules converted per 100 ev) for oxalic range from 4 to 6; for formic acid the values are 2.5 for electrons and 1.7 for deuterons.

INTRODUCTION

Aliphatic carboxylic acids are readily oxidized, and undoubtedly in solutions containing radioactivity they all will be oxidized to an extent depending on the amount of radiation. This paper reports an investigation of radiation effects on aqueous solutions of two of these compounds, formic and oxalic acids.

At low levels of radiation intensity the total amount of change is small. However, at high levels of radioactivity, expected changes are appreciable. Radiation-induced changes of both formic and oxalic acids have been reported in the literature, but the work was done at relatively low radiation intensities. One purpose of the present study was to determine whether the radiation yield would remain constant over the range from low to very high intensities. For convenience of comparison, prior literature values are included in the discussion of the results of this paper.

EXPERIMENTAL

Effects of Radiation on Formic Acid*

Aqueous solutions of pure formic acid, may by dilution of Reagent-Grade material, without any effort to eliminate air, were exposed to both deuterons and electrons. Only electron irradiation was used on the two solutions containing both uranyl nitrate hexahydrate (UNH) and formic acid. The deuteron exposures were made in a glass cell having a thin mica window. The technique of such cyclotron exposures is discussed by Bowman and Treiman.¹ The electron irradiations were made using high voltage irradiations from a Van de Graaf generator. These irradiations were made in a water-cooled glass cell having the characteristics reported by Safford.² Table 1 contains data on the effects obtained. Similar data, obtained with electron irradiation alone, are reported by Germany and Kay.³

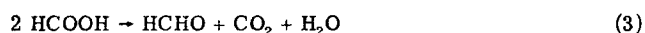
* Work performed by A. Germany and W. L. Kay.

Table 1. Effect of 1.4 mv electrons and mv (effective) deuterons on formic acid in aqueous solution.

Irradiation Kind	Time (hr)	Current (μ a)	Original acid normality	Original reducing normality	Original % UNH	Residual acid after bombardment (%)	Reducing power after bombardment (%)
d	0.5	0.5	1.032	2.048	0	95.4	94.3*
d	0.5	2.0	1.032	2.048	0	80.9	81.1
e	0.33	0.5	0.598	1.183	0	89.4	87.8*
e	0.5	0.5	0.598	1.183	0	94.2	92.8
e	0.5	0.5	--	0.127	20	--	65.7
e	0.5	0.5	--	0.1185	40	--	79.8

* Possible mechanical solution loss.

For discussion of results it is convenient to define a quantity $G(x)$ as the number of molecules of substance (x) either formed or destroyed per 100 electron volts expended by radiation. From Table 1, $G(\text{HCOOH destroyed}) = \sim 2.5$ for electrons and ~ 1.7 for deuterons. Since the titration of the irradiated samples with base and KMnO_4 gave about equal values, oxalic acid is not an important product under these conditions, being formed in quantities equivalent to $\sim 1/10$ of the amount of HCOOH destroyed. Kailan^{4,5} used betas and gammas from approximately 100 mg of radium on a 0.01M formic acid solution, pH = 2.5. His results correspond to $G(\text{HCOOH destroyed}) = 2$ and $G(\text{C}_2\text{O}_4^{2-} \text{ formed}) = 1.2$. Fricke, Hart, and Smith⁶ work with x radiation of effective wavelength of 0.35 A at an intensity of 500 to 2000 r/min acting on both air-free and oxygen-containing solutions. Values estimated from their results in air-free 1M formic acid (pH adjusted to 2) are $G(\text{H}_2 \text{ formed}) = 3.3$ and $G(\text{CO}_2 \text{ formed}) = 8.6$.* They gave data which can be summed up conveniently by consideration of the following three equations:



They state reaction 1 and/or 2 occur at constant rate at all pH values, with an additional reaction, 3, liberating CO_2 occurrent in more concentrated acid solutions (0.005 to 1M).

Effect of X-ray Radiation on Oxalic Acid

Only x radiation was used in this investigation. Operating level for the 0.06M solution was $\sim 3.3 \times 10^4$ r/min; the corresponding figure for the 0.4M solution was 3×10^2 r/min.

The radiation cone in front of the gold target of the Notre Dame generator (operating at 2.3 mv) was explored with a Victoreen r-meter and positions were noted corresponding to the values listed in Table 2. For the higher r values, particularly, this method of monitoring gives uncertain results.†

* The oxygen-containing solutions which Fricke, Hart, and Smith studied were 10^{-3} M or less in formic acid; for such solutions the yields of hydrogen and carbon dioxide were somewhat diminished.

† An improved method has been developed recently by Wiedenbeck.⁷

For example, the chamber measures only up to 250 r but intensities of $\sim 50,000$ r/min are obtained at a $100 \mu\text{a}$ electron current. The method of monitoring for this value is to operate the generator at $1 \mu\text{a}$ for thirty seconds. However, errors of reading the microammeter during this interval (when the current is still variable) make accuracies of greater than $\pm 20\%$ improbable. Similar inaccuracy may be present in the 25,000 r/min points; the values of 10,000 r/min may be in error by $\pm 10\%$ and the smaller values by $\pm 5\%$.

Because of geometry there was only one position corresponding to 50,000 r/min, but it was possible to select two positions for each of the other values. After establishment of the 50,000 r/min point, a water filled test tube (1.6 mm diameter) was suspended so that the liquid column was bisected by the horizontal midplane of the radiation cone. The 25,000 r/min positions were then established and water-filled tubes were suspended at these points. The process was repeated to determine the 10,000 r/min points, etc.

With the method of suspension employed in the monitoring, 13 tubes could be exposed simultaneously to a known total irradiation. The procedure was to pipet 10-ml portions of the test solution into the test tubes, stopper them, and irradiate them all simultaneously at the previously calibrated positions. After the 30-minute run, the tubes were removed and the contents analyzed. For the 25,000 r/min positions, the amount of solution irradiated was reduced to ~ 3 ml to conform to the smaller beam area.

Table 2. Effects of 30-minute X-ray irradiation on aqueous oxalic acid solutions.

$(\text{COOH})_2$ (M)	Total r units	Avg decrease in acid titre (%)	Number of irradiations
0.06	1.5×10^6	13.8*	3
	7.5×10^5	(2.7 and 5.0)†	2
	3×10^5	0.8	2
	3.3×10^4	1.1	2
	1.7×10^4	(1.0 and 0.1)†	2
	9×10^3	1.3	2
	4.5×10^3	0	2
0.40	1.5×10^6	1.3	1
	7.5×10^5	0.8	2
	3×10^5	0	2
	3.3×10^4	0	2
	1.7×10^4	0	2
	9×10^3	0	2
	4.5×10^3	0	2

* This solution gave 11.8% decrease in KMnO_4 titration.

† Divergent values from separate irradiations. In other cases, deviations obtained in separate experiments differed by no more than a factor of 1.1.

One ml of the irradiated solution was pipetted into 5 ml of water and the solution heated to 50°C. Duplicate samples were titrated to a phenolphthalein end-point with sodium hydroxide, using a micro-buret. The analyses for the 0.06M solution have a precision of about 0.5% and those for the 0.40M solution about 0.3%. Comparison of acid titre before and after irradiation yielded the values listed in Table 2.

The data given are sufficient only for a rough calculation of G. For the 0.06M and 0.40M solutions the value of G(H₂C₂O₄ destroyed) are ~4 and ~6, respectively. Fricke, Hart, and Smith⁶ studied air-free solutions of oxalic acid at various concentrations irradiated at 500 to 2000 r/min. At 0.1M (pH adjusted to 3), their results correspond roughly to G(H₂ formed) = 0.57 and G(CO₂ formed) = 7.6. They state that at low concentrations (<10⁻²M) the reaction



proceeds exclusively, but at higher concentrations the yield of CO₂ increases and the H₂ yield decreases. Fricke, Hart, and Smith suppose that this trend is caused by the increasing importance of the overall reaction



accompanied simultaneously by the suppression of overall reaction.⁴

It is noteworthy that at the lowest concentration they studied G(CO₂ formed) had dropped to roughly 3.6 while G(H₂ formed) had increased to 1.8.

The relative extent of overall reactions 4 and 5 in the present experiments may be estimated from a comparison of the acid and permanganate titrations given by the first experiment in Table 2. Conversion of one molecule of (COOH)₂ to one molecule of HCOOH does not change the reducing normality of the solution, but decreases the acid normality to one-half. We find that the ratio, molecules HCOOH formed : molecules (COOH)₂ destroyed, equals ~0.25, while the value obtained from the data of Fricke, Hart, and Smith for 0.1M solution is 0.92.

Kailan^{4,5} working with betas and gammas from approximately 100 mg of radium acting on 0.02M air-saturated solutions, obtained results corresponding to G(H₂C₂O₄ destroyed) = 0.8 and a value of 0.4 for the ratio indicated. The discrepancy with the value of G obtained in the present work may indicate an intensity effect, but more probably arises from imperfect monitoring methods employed by Kailan.

DISCUSSION

In any aqueous solution, the energy of the ionizing radiation is absorbed chiefly by the water, because it is present in much larger amounts than any other component. The water is thereby decomposed to reactive free radicals, H and OH, which may react chemically with substances dissolved in the water.⁸ The primary yield of radicals formed from the water per unit of energy input will be independent of the intensity of the radiation. With such reactive solutes as organic molecules present, it is believed that a large fraction of the primarily-formed radicals undergo reactions with the solute. The yield, G, for destruction of solute molecules should therefore depend only to a minor degree on the radiation intensity. The present work confirms this expectation, in that the values of G obtained for destruction of oxalic and formic acids were of the same order of magnitude as those reported in the literature for much lower radiation intensities.

The work was not sufficiently extensive to contribute essentially to an understanding of the details of the reaction mechanisms. A discussion of mechanisms, based on literature reports on a large number of organic compounds in solution, is given elsewhere in this record.⁸