

CCA-290

541.15:547.821:546.723-226

The Radiation Chemistry of Deaerated Aqueous Vinylpyridine Sulphate — Ferric Sulphate Solutions*

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Received January 18, 1963

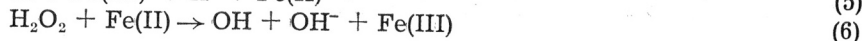
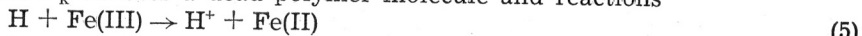
The mechanism of radiation-chemical reactions of deaerated aqueous vinylpyridine sulphate solutions irradiated with Co-60 gamma rays in the presence and absence of ferric sulphate have been investigated. The effects of vinylpyridine sulphate concentrations and sulphuric acid on $G(\text{H}_2\text{O}_2)$ and including ferric sulphate on $G(\text{H}_2)$ and $G(\text{Fe}^{2+})$ have been measured. A maximum value in $G(\text{H}_2\text{O}_2)$ at vinylpyridine sulphate concentrations about $4 \cdot 10^{-3} M$ was observed, but only a plateau was obtained in $G(\text{H}_2)$ at vinylpyridine sulphate concentrations below $10^{-3} M$. High vinylpyridine sulphate and sulphuric acid concentrations decrease $G(\text{H}_2\text{O}_2)$ and $G(\text{H}_2)$, which is decreased by ferric sulphate too, but its efficiency depends on the sulphuric acid concentration. $G(\text{Fe}^{2+})$ increases to a maximum value with increasing vinylpyridine sulphate and ferric sulphate concentrations, but decreases with increasing sulphuric acid concentrations. From the experimental results $G(\text{H})$ and $G(\text{OH})$ values were calculated. These and other results in this system are discussed to explain the mechanism of radiation-chemical reactions.

INTRODUCTION

The effects of ionising radiations on aqueous solutions are usually interpreted in terms of the formation of the primary products H , OH , H_2 and H_2O_2 . Vinylpyridine sulphate (abbr. VP) reacts with H and OH radicals to form vinylpyridine sulphate radicals (abbr. R_k). These reduce ferric ions in aqueous solutions. The following reactions are important:



where P_k denotes a dead polymer molecule and reactions

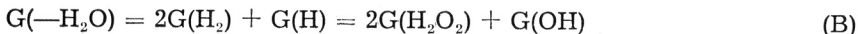


When these reactions are the only processes involving the vinylpyridine sulphate we may write

$$G(\text{Fe}^{2+}) = G(\text{H}) + G(\text{OH}) \quad (\text{A})$$

* Paper presented at the Second International Congress of Radiation Research, Harrogate, England, August 5th — 11th, 1962.

and by the application of the stoichiometric equation for the water decomposition



$G(\text{H})$ and $G(\text{OH})$ can be evaluated from the following equations

$$G(\text{H}) = \frac{1}{2} G(\text{Fe}^{2+}) + G(\text{H}_2\text{O}_2) - G(\text{H}_2) \quad (\text{C})$$

$$G(\text{OH}) = \frac{1}{2} G(\text{Fe}^{2+}) + G(\text{H}_2) - G(\text{H}_2\text{O}_2) \quad (\text{D})$$

EXPERIMENTAL

Materials

Because same results were obtained with water treated as recommended by Baxendale¹ and once distilled pipewater redistilled from a quartz bidistillator, such triple distilled water was used to make up all solutions. Vinylpyridine of *p. a.* grade was purified by vacuum distillation. Vinylpyridine sulphate was prepared by adding to a known amount of vinylpyridine the necessary equivalent quantity of diluted sulphuric acid to form the salt. Ferric solutions were made up using *p. a.* grade ferric sulphate.

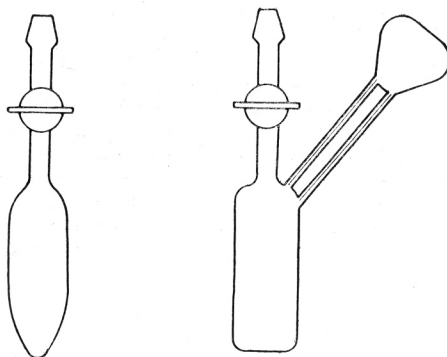


Fig. 1. Irradiation cells.

Analyses

Ferrous ion concentrations were determined spectrophotometrically with *o*-phenanthroline by absorption at 510 m μ and pH 4.6². The procedure recommended by Saldick and Allen² was applied and sodium fluoride added to complex the ferric ions.

Hydrogen peroxide concentrations were measured spectrophotometrically by Eisenberg's method³ with titanium sulphate by absorption at 410 m μ in 1.5 to 3.5 normal sulphuric acid solutions.

Molecular hydrogen measurements were made with a slightly modified apparatus according to Allen⁴ and Bonet-Maury⁵.

Deaeration procedure

Samples were three times deaerated by the freezing-pumping-thawing procedure similar to that used by Weiss⁶ and Allen⁴.

Dose measurements

Dose measurements were carried out by means of the Fricke dosimeter using the value of $G(\text{Fe}^{2+})$ 15.5 ± 0.3 .

Irradiation facilities

The source of ionizing radiation used in these experiments was a 300 curie Co-60 »swimming pool« type irradiation facility. The absorption of the radiation was reasonably uniform ($\pm 5\%$) throughout the irradiated samples and had an average value of 1.5×10^{15} eV. ml⁻¹. sec⁻¹ for water. Two types of irradiation cells were used, one for the determination of ferrous ion and hydrogen peroxide yields

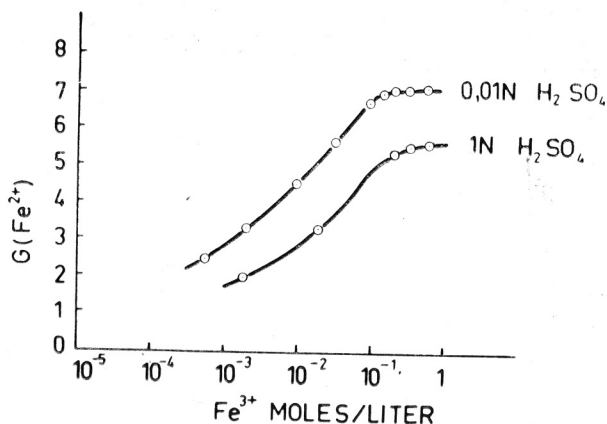


Fig. 2. Dependence of $G(\text{Fe}^{2+})$ upon ferric sulphate concentration in 0.01 N and 1 N sulphuric acid solution. Vinylpyridine sulphate concentration 4.0×10^{-3} moles/liter.

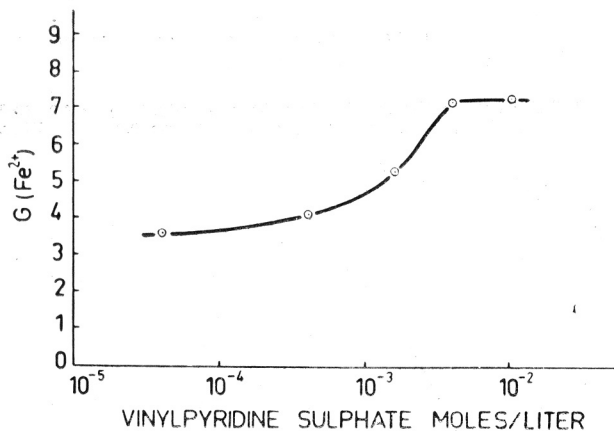


Fig. 3. Dependence of $G(\text{Fe}^{2+})$ upon the vinylpyridine sulphate concentration in 0.01 N sulphuric acid solution. Ferric sulphate concentration 0.2 moles/liter.

and a second one with side arms for the determination of hydrogen gas yields (Fig. 1). In the last one solutions were irradiated in the bulb filled to a point about halfway up the capillary tubes. In the small cross section of the capillaries diffusion of the gas was so slow, that no measureable amount of gas was lost or gained by the solution during experiments.

RESULTS AND DISCUSSION

Ferrous ion yields. The $G(\text{Fe}^{2+})$ yields depend on the vinylpyridine sulphate, ferric sulphate and sulphuric acid concentrations. The results in Fig. 2 and 3 show that $G(\text{Fe}^{2+})$ increases with increasing ferric sulphate and vinylpyridine sulphate concentrations to a maximum value of 7.2 in 0.01 *N* and 5.7 in 1 *N* sulphuric acid solutions. The decreasing $G(\text{Fe}^{2+})$ yield in Fig. 4 shows that the proportion of radicals reacting with the vinylpyridine sulphate decreases with increasing sulphuric acid concentrations.

According to Allen^{7,8} and Sworski^{9,10} in sulphuric acid solutions the following reactions are possible

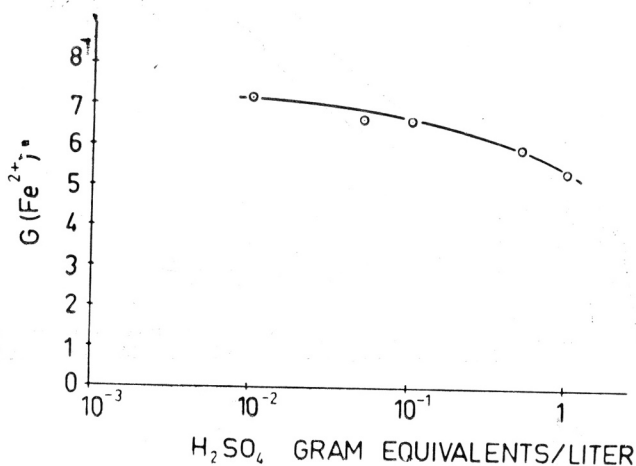


Fig. 4. Dependence of $G(\text{Fe}^{2+})$ upon the sulphuric acid concentration in 4.0×10^{-3} *M* vinylpyridine sulphate solution. Ferric sulphate concentration 0.2 moles/liter.

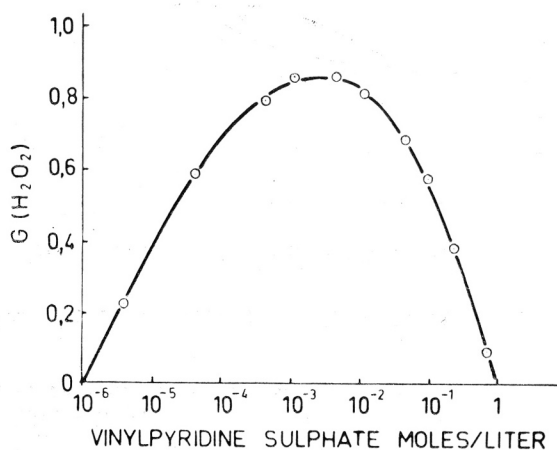


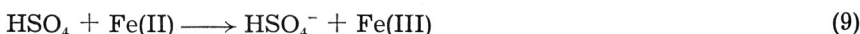
Fig. 5. Dependence of $G(\text{H}_2\text{O}_2)$ upon the vinylpyridine sulphate concentration in 0.01 *N* sulphuric acid solution.



and perhaps also



The decrease in $G(\text{Fe}^{2+})$ with increasing sulphuric acid concentrations could therefore be explained by reactions (7) and (8), followed by the reactions of the bisulphate radicals and perhaps also sulphate ion radicals with ferrous ions formed during irradiation.



and perhaps also



The calculation of primary radical yields $G(\text{H})$ and $G(\text{OH})$ from experimental $G(\text{Fe}^{2+})$, $G(\text{H}_2\text{O}_2)$ and $G(\text{H}_2)$ values by means of equations (C) and (D) is therefore justified only at those sulphuric acid concentrations where reactions (7) and (8) may be neglected.

Hydrogen peroxide yields. The results in Fig. 5 and 6 show that $G(\text{H}_2\text{O}_2)$ depends both on vinylpyridine sulphate and sulphuric acid concentrations. The outstanding features are: $G(\text{H}_2\text{O}_2)$ has a maxima value of 0.88 at vinylpyridine sulphate concentrations about $4 \times 10^{-3} M$; $G(\text{H}_2\text{O}_2)$ decreases with increasing sulphuric acid concentrations.

$G(\text{H}_2\text{O}_2)$ increases at low vinylpyridine sulphate concentrations because the following back reaction is gradually inhibited



by reaction



and decreases when the concentration of the vinylpyridine sulphate is high enough to react with the hydrogen peroxide precursors, thereby diminishing $G(\text{H}_2\text{O}_2)$ yields. A similar explanation was given by Collinson *et. al.*¹¹ for the $G(\text{H}_2\text{O}_2)$ yields in the acrylamide system.

In $4 \times 10^{-3} M$ vinylpyridine sulphate solutions, as shown in Fig. 6, $G(\text{H}_2\text{O}_2)$ decreases with increasing sulphuric acid concentrations from 0.88 in 0.01 *N* to 0.61 in 2 *N* sulphuric acid solutions. This can be explained by the reaction of bisulphate and perhaps also sulphate ions with hydrogen peroxide precursors, thereby diminishing $G(\text{H}_2\text{O}_2)$ yields. This explanation is in accordance with Allen^{7,8} and Sworski^{9,10} who postulated the possibility of reactions (7) and (8).

Molecular hydrogen yields. The results in Fig. 7 and 8 show that $G(\text{H}_2)$ is decreased by vinylpyridine sulphate and ferric sulphate. The decrease in $G(\text{H}_2)$ is accounted for by an increase in the reaction of vinylpyridine sulphate and ferric sulphate with molecular hydrogen precursors, for example by the reactions



and



The fractional lowering of molecular hydrogen yields plotted against $\log(VP \times 4 \times 10^{-2})$ fits in its general trend the Schwarz type plot given by Allen¹².

Fig. 8 shows that efficiency of ferric sulphate to diminish $G(H_2)$ falls off with increasing sulphuric acid concentrations and is about 7 times less efficient in 1 N than in 0.01 N sulphuric acid solutions. This is in accordance with the results of Schwarz¹³ who found that $Fe(OH)^{2+}$ and $Fe_2(OH)_2^{4+}$ ferric-iron complexes are more effective in removing H radicals than $FeSO_4^+$

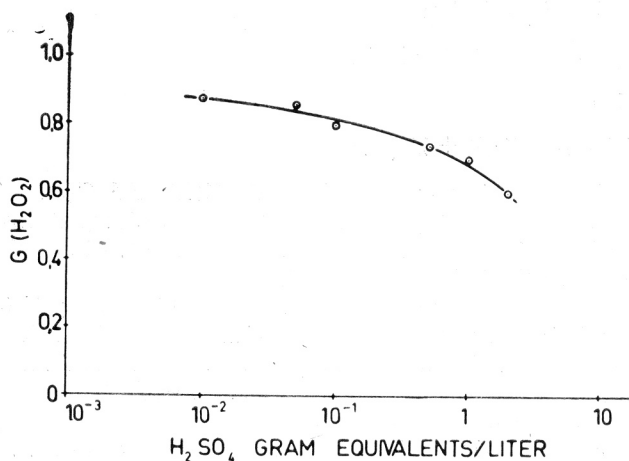


Fig. 6. Dependence of $G(H_2O_2)$ upon the sulphuric acid concentration in $4.0 \times 10^{-3} M$ vinylpyridine sulphate solution.

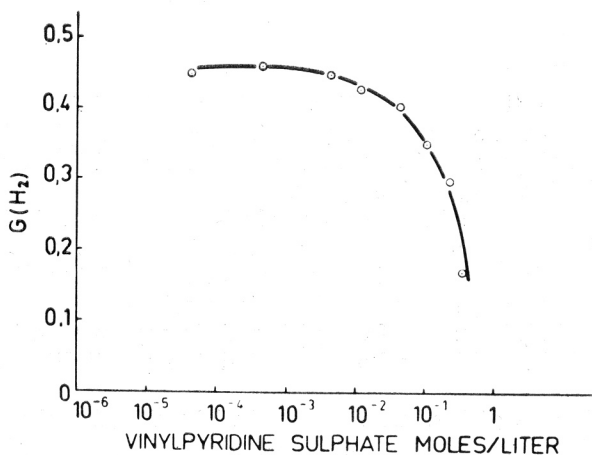


Fig. 7. Dependence of $G(H_2)$ upon the vinylpyridine sulphate concentration in 0.01 N sulphuric acid solution.

complexes. From their reported formation constants we calculated the amount of total ferric-iron present in the form of various complexes. Thus in 0.1 M ferric sulphate solutions in 0.01 N sulphuric acid there is present 3.98% $Fe(OH)^{2+}$, 74.7% $Fe_2(OH)_2^{4+}$, 6.39% $FeSO_4^+$, 9.38% $Fe(SO_4)_2^-$ and 5.55% Fe^{3+} ,

whereas in 1 N sulphuric acid solution there are present: 2.0% $\text{Fe}(\text{OH})^{2+}$, 5.6% $\text{Fe}_2(\text{OH})_2^{4+}$, 51.5% FeSO_4^+ , 33.25% $\text{Fe}(\text{SO}_4)_2^-$ and 7.65% Fe^{3+} . It is evident that the concentration of the more reactive species is higher in 0.01 N sulphuric acid than in 1 N sulphuric acid solution.

$G(\text{H}_2)$ yields in Fig. 8 at ferric ion concentrations below 0.01 M Fe^{3+} confirm the known fact that $G(\text{H}_2)$ is decreased by increasing sulphuric acid concentrations¹⁴.

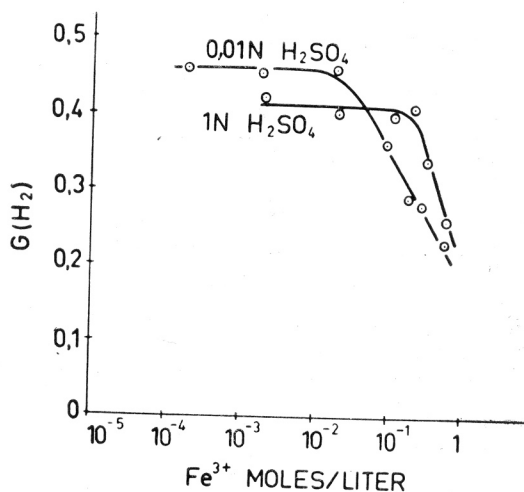


Fig. 8. Dependence of $G(\text{H}_2)$ upon the ferric sulphate concentration in 0.01 N and 0.1 N sulphuric acid solution. Vinylpyridine sulphate concentration 4.0×10^{-3} moles/liter.

Primary radical yields: As reactions (7) and (8) may be neglected only up to approximately 0.01 N sulphuric acid concentration, $G(\text{H})$ and $G(\text{OH})$ yields have been calculated for 0.01 N sulphuric acid solutions. Experimental $G(\text{Fe}^{2+})$ values corrected for the increase by reaction of ferric ions with molecular hydrogen precursors were used in equations (C) and (D). Calculated radical yields are

$$0.01 \text{ N } \text{H}_2\text{SO}_4 : G(\text{H}) = 3.85 \pm 0.14 \quad G(\text{OH}) = 3.02 \pm 0.14$$

CONCLUSIONS

The experimental results show the following outstanding features: (1) The effects of sulphuric acid concentrations on $G(\text{Fe}^{2+})$ show, that bisulphate and perhaps also sulphate ions may react, with OH radicals or some equivalent species. (2) $G(\text{H}_2)$ is decreased by ferric ions, but their efficiency falls off with increasing sulphuric acid concentrations. (3) $G(\text{H}_2\text{O}_2)$ decreases with increasing sulphuric acid concentrations indicating that reaction of bisulphate ions and perhaps also sulphate ions with hydrogen peroxide precursors is taking place. (4) A maximum value in $G(\text{H}_2\text{O}_2)$ at vinylpyridine sulphate concentrations about 4×10^{-3} M was observed indicating that the back reaction of hydrogen peroxide with H radicals is inhibited by vinylpyridine sulphate.

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IZVOD

Radijaciona kemija deaeriranih vodenih otopina vinilpiridinsulfata i ferisulfata

B. Čerček

Istraživani su mehanizmi radiacijono-hemijskih reakcija u deaeriranim vodenim otopinama sistema vinilpiridinsulfat - ferisulfat — sumporna kiselina. Otopine su ozračivane gama zracima Co-60. Ispitani su koncentracijski efekti vinilpiridinsulfata i sumporne kiseline na $G(H_2O_2)$ i uključujući ferisulfat na $G(H_2)$ i $G(Fe^{2+})$. Utvrđen je maksimum za $G(H_2O_2)$ kod koncentracija vinilpiridinsulfata približno $4 \cdot 10^{-3} M$, dok je za $G(H_2)$ dobijen samo plateau kod koncentracija vinilpiridinsulfata ispod $10^{-3} M$. Visoke koncentracije vinilpiridinsulfata i sumporne kiseline smanjuju $G(H_2)$ i $G(H_2O_2)$. $G(H_2)$ smanjuje se takođe visokim koncentracijama ferisulfata, međutim njegova efektivnost pada porastom koncentracije sumporne kiseline. Porastom koncentracije vinilpiridinsulfata i ferisulfata $G(Fe^{2+})$ približava se maksimalnoj vrednosti, koja opada rastućom koncentracijom sumporne kiseline. Upotrebom dobijenih eksperimentalnih rezultata izračunate su vrednosti za $G(H)$ i $G(OH)$. Na osnovu ovih i drugih eksperimentalnih rezultata izvedeni su zaključci o mehanizmu radiacijono-hemijskih reakcija.

ODJEL RADIJACIONE KEMIJE
 INSTITUT »JOZEF STEFAN«
 LJUBLJANA

Primljeno 18. siječnja 1963.