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DOSIMETRY STUDIES AND RADIOLYSIS OF AQUEOUS SOLUTIONS OF CHLORAL HYDRATE

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ABSTRACT

The radicals involved in the radiolysis of 0.2 M aqueous solutions of Chloral hydrate are identified by means of the electron paramagnetic resonance and mass spectrometry data of irradiated polycrystalline powder and single crystals of Chloral hydrate.

Dosimetry studies were also done with aqueous solutions of Chloral hydrate at several molar concentrations. The variation of pH of the irradiated solutions with dose may be used as a dosimetric relation in the 10 to 700 rads dose interval with good accuracy.

RESUMEN

Los radicales intermediarios de las reacciones inducidas por la radiación ionizante en soluciones acuosas 0.2 M de Cloral hidratado son identificados a partir de los datos obtenidos de la resonancia paramagnética electrónica y de espectrometría de masas de polvo policristalino y monocristales de Cloral hidratado irradiados.

También fueron realizados estudios dosimétricos con soluciones acuosas de Cloral hidratado a diversas concentraciones molares. La variación del pH de las soluciones irradiadas con la dosis puede ser empleada como una relación dosimétrica en el intervalo de 10 a 700 rads con buena precisión.

RADIOLYSIS OF AQUEOUS SOLUTIONS OF CHLORAL HYDRATE.

The Radiation Chemistry of aqueous solutions of Chloral hydrate has been studied in the past by Andrews[1], Sugimoto[2] and Spinks, et al[3, 4, 5]. McIntosh[5] proposed the following mechanism for the radiolysis:

$$
\begin{array}{llr}
H_2O & \xrightarrow{\ \ I\ \ } \dot{R} & (1) \\
\dot{R} + S & \longrightarrow \dot{S} + R & (2) \\
\dot{S} + O_2 & \longrightarrow \dot{S}O_2 & (3) \\
\dot{S}O_2 & \longrightarrow 3\ \text{acid} + \dot{R} & (4) \\
\dot{R} + \dot{S} & \xrightarrow{H_2O} \text{stable product (or products)} & (5)
\end{array}
$$

where I is the dose rate, R is very likely $\cdot H$ or $\cdot OH$, or even both, S represents a molecule of Chloral hydrate, a dot over a symbol representing a free radical, and "acid" corresponds to HCl.

The primary interaction of the radiation with water in dilute aqueous solutions as postulated in (1) is generally accepted. The reactions (2), (3) and (4) form a chain mechanism which is consistent with the large G (HCl) values observed by several authors (references 1 to 5) and with our observations[6] of the considerable variation in pH of the irradiated solutions between 10 rads to 1.5 Mrads.

Some deductions about the radical $\dot{S}$ may be done from a consideration of the overall activation energy for the production of acid. According to McIntosh[5], it may be speculated, -since the overall activation energy for the Chloral hydrate radiolysis is less, or at the most, equal to that for Bromal hydrate[3, 4, 7]-, that the free radical $\dot{S}$ has resulted from an attack on the aldehyde end of the Chloral hydrate molecule by $\dot{R}$. If the attack was on the halogen end of the molecule, the activation energy for the production of acid would be higher for Chloral hydrate solution because the C-Cl bond strength is greater than that for the C-Br bond. Radical $\dot{S}$ has not been identified and that is the purpose of this part of the paper.

Polycrystalline powder of Chloral hydrate (Baker, 1568) was irradiated with 1.0 MeV electrons, in air, at room temperature, in a 1 mm thickness layer, using the Electron Van de Graaff Accelerator at the Instituto de Física, UNAM. Dose rate was determined with the relation:

$$(D.\,R.)_s = \frac{m^S s}{m^S d}\,(D.\,R.)_d \qquad (6)$$

where $(D.\,R.)_s$ and $(D.\,R.)_d$ are the dose rate for the sample and dosimeter respectively. We used as dosimeter the powder of Cobalt-activated borosilicate glass (CABS), for which a dose-ESR signal intensity relation has been obtained by a method described before[8]. The mass stopping powers fraction $m^S s\,/\,m^S d$ has a value of 0.99, calculated from the formal definition[9], according to the data of Henricksen[10] and using the following values of the appropriate constants:

	CABS	Chloral hydrate
Mean density (g/cc)	2.266	1.908
Effective atomic number	9.337	8.2
Mean number of atoms per cc (X 10^{23})	0.737	0.696
Mean ionization potential (eV)	126.9	111.5

Electron irradiation induces paramagnetic species in polycrystalline Chloral hydrate, caracterized by the ESR spectrum shown in figure 1. The ESR determination was made at room temperature using the Varian 4502-15 EPR spectrometer at the Instituto de Física, UNAM, operating at a microwave frequency in the X-band near 9.4 GHz with 100 KHz field modulation.

The concentration of paramagnetic species varies with dose according to the relation plotted in figure 2. Three kinds of behavior are in evidence: firstly, the formation of paramagnetic species in the range up to 40 Krads; secondly, the sublimation of the irradiated samples and reactions between active species induced by irradiation to form HCl and other products as was reported by Platford[4], and finally, a saturation in which equilibrium sets in between the reactions and the formation of paramagnetic species.

Because the time decay of the induced paramagnetic species at room temperature is slow, as shown in figure 3, there is negligible loss of the number of paramagnetic species during the time necessary to prepare a solution. Hence it is possible to compare the variation in pH with dose of the solution prepared with the irradiated powder with that for the irradiated Chloral hydrate solution.

Aqueous solutions were prepared with distilled (pH = 5.85) and tridistilled water (pH = 6.12), which was then further purified by distilling first from an alkaline permanganate solution and then from an acidic dichromate solution.

The solutions were irradiated with 1.0 MeV electrons, at room temperature, placing 7cc in Petri dishes on a rotating array as described by Adem[11]. The sample thickness was about 3 mm. Dose rate was calculated using relation (6). $(D.R.)_d$ was determined by means of the Fricke method[12], using[13] $G(Fe^{3+}) = 15.45 \pm 0.11$.

The pH variation of the solutions prepared with the irradiated powder was found to behave in the same way as that of the irradiated solutions as can be seen in figure 4. These graphs cannot be compared directly because for the solutions prepared with irradiated powder, the radiation absorbed energy forms only the paramagnetic species that react with water when the solution is prepared. The considerable pH variation is explained if the paramagnetic species react through the chain mechanism of reactions (2) to (4).

Due to the difficulty of obtaining further information from the irradiated polycrystalline ESR spectra, it was necessary to prepare a single crystals of Chloral hydrate.

Small Chloral hydrate "leafs" about 3 to 5 mm large were obtained by evaporation over copper from molten Chloral hydrate at 48 ± 0.1 °C after 48 to 72 hours. Chloral hydrate could also be recrystallized from a Chloroform solution, but upon repeated recrystallization hexagonal tabular crystals come to grow slowly. After 48 to 72 hours the single crystals grow to sizes of 2 to 3 mm in diameter.

The irradiated single crystals maintained in normal ESR sample holders were placed in a cavity (Varian 4533) that could be rotated so as to enable the variation of the magnetic field direction with respect to the crystal planes. In this way it was possible to get more resolution on the spectra lines.

ESR spectra is composed of several lines, as is shown in figure 5, where several spectra were necessary to draw to identify the paramagnetic species. The initial distribution observed for low magnetic field values in spectra 1, 2 and 4 establishes an intensity sequence of 1:4:8:12:15:16:16:15:12:8:4:1 that was assumed to correspond to the $CCl_3\dot{C}(OH)_2$ radical, where the unpaired electron interacts with 3 equivalent Chlorine atoms and 2 equivalent protons. A second sequence is also observed, 1:5:12:20:26:26:20:12:5:1, that was assumed to correspond to the $\dot{C}Cl_2CH(OH)_2$ radical, with the unpaired electron interacting with a proton, 2 equivalent Chlorine atoms and 2 equivalent protons, hydroxyls. Unfortunately it was only possible to evaluate the initial intensity sequence in both cases, due mainly to poor uniform resolution of spectra through the magnetic field scanning. However, our ESR information is enough to establish the existence of these two radicals.

Mass spectrograms (MS) were also obtained for irradiated and non-irradiated samples, using the Hitachi Perkin-Elmer RMU-6D Mass Spectrometer at the Instituto de Química, UNAM. Table I presents the relative abundances of the main ion found for irradiated and non-irradiated samples with respect to mass 82.

From the $[H_2O]^+$ ion relative abundance in both samples it is determined that irradiation induces deshydration of Chloral hydrate.

The production of HCl observed by Platford[4] in the irradiation of solid Chloral hydrate may be explained by reaction (7) (see collection of reactions Table II). By this mechanism the formation of the $CCl_3\dot{C}(OH)_2$ radical by irradiation may explain the interaction of the unpaired electron with 3 equivalent Chlorine atoms and 2 equivalent protons observed in the ESR spectra. Upon solution this radical reacts with water (reaction 8) giving another radical, $\dot{C}Cl_2$-COOH and HCl. This second radical reacts with water (reaction 9) to give $CHCl_2$-COOH or $CCl_2\dot{C}(OH)_2$ and $\cdot OH$, which may react with the Chloral hydrate molecule to give again the $\dot{C}Cl_2$ COOH radical and HCl (reaction 10) and started the proposed chain mechanism. The product $CHCl_2$COOH contributes to the acidity of the solution that changes its pH value as is observed in figure 4.

The radical $\dot{C}Cl_2CH(OH)_2$ may be formed with the irradiation through (reaction 11) giving place to Chlorine atoms. The relative abundance of Chlorine ions observed in the MS of non-irradiated and irradiated samples (Table I) is explained by means of this mechanism. The abundance for the irradiated sample is lower than in the case of the non-irradiated sample. In solution, the $\dot{C}Cl_2CH(OH)_2$ radical reacts (12) with water to form the $\dot{C}Cl_2$COOH radical, HCl, H_2 and $\cdot OH$ which react as was explained in reactions (7) to (10). It is also interesting to note that the $\dot{C}Cl_2$COOH radical is deshydrated (13) in the mass spectrometer pre-heater to give the $\dot{C}Cl_2$CHO radical that when it is ionized gives the $\overset{+}{C}Cl_2CHO$ ion with relative abundance greater in the irradiated sample than in the non-irradiated, as is expected.

In solution, under $\cdot OH$ activity, reaction (10) takes place, as was obtained by Dixon[15]. He based his interpretation on the ESR spectra of the $\dot{C}Cl_2COOH$ radical in solution.

However, the radicals $CCl_3\dot{C}(OH)_2$ and $\dot{C}Cl_2CH(OH)_2$ explain the ESR data, and reactions (7) to (12) explain the mechanism of the radiolysis of aqueous solutions of Chloral hydrate through the CCl_2COOH radical.

DOSIMETRY STUDIES

In irradiation of biological systems one of the main considerations is the determination of absorbed dose with adequate precission.

For X or gamma radiation, the determination of absorbed dose can be done using the expression

$$D_s = \frac{\overline{(\mu/\rho)_s}}{\overline{(\mu/\rho)_d}} D_d \tag{14}$$

where D_s and D_d are the doses, $\overline{(\mu/\rho)_s}$ and $\overline{(\mu/\rho)_d}$ the mean mass energy absorption coefficients for the system and dosimeter respectively.

D_d can be determined using a secondary dosimeter, with physical and geometrical characteristics similar to the system. The values of the coefficients can be calculated from data of the radiation source, system and dosimeter.

In particular, when ^{60}Co gamma radiation is used, with mean energy of 1.25 MeV, relation (14) can be replaced by

$$D_s = \frac{\overline{(Z/A)_s}}{\overline{(Z/A)_d}} D_d \tag{15}$$

where $\overline{(Z/A)_s}$ and $\overline{(Z/A)_d}$ are the mean electron densities of the system and dosimeter respectively.

For heterogeneous materials, the value of $\overline{(Z/A)}$ can be calculated from

$$\overline{(Z/A)} = \sum_i \omega_i \, (Z/A)_i$$

where ω_i is the weigth fraction and $(Z/A)_i$ the electron density of the ith element in the medium.

In the case of X-rays with a known energy spectrum the radiation beam can be considered as the sum of mono-energetic beams that are absorbed independently by the material. The mean coefficient is a function of the energies and of the number of photons in each energy range. If the spectrum and the variation of the coefficient with energy are known, both can be combined graphically to obtain the mean coefficient for each of the materials, because

$$\overline{(\mu/\rho)} = \sum_i \omega_i \, (\mu/\rho)_i$$

where $(\mu/\rho)_i$ is the mass coefficient for the ith element in the medium.

Several primary and secondary dosimeters have been used to determine the value of D_d for biological systems, but in the case of low level radiation sources it is still necessary to develop a secondary dosimeter with characteristics similar to biological systems, especially in the case of X-rays irradiations.

It has been founded by Boyd[16] and Sugimoto[2] that aqueous solutions of Chloral hydrate can be used as a secondary dosimeter for low level doses.

The purposes of this part of the paper are: firstly, to study the effect of ^{60}Co gamma radiation, up to 1.0 MeV X-rays and 1.0 MeV electrons on aqueous solutions of Chloral hydrate at several concentrations. Secondly, to find some relations between the pH variation and dose in several dose intervals.

The 1.0 MeV electron irradiations were performed as was described before. Bremsstrahlung X-rays were obtained from the gold target array[17] of the Accelerator and the solutions exposed in a 5cc Kimax tubes with bakelite screwtops in the form described in detail by Limón[6].

A 3500 Ci of ^{60}Co Gammacell 200 (Atomic Energy of Canada Ltd.) of the Laboratorio Nuclear, UNAM, was used for gamma irradiations, using the same container as in X-rays experiments placed at a special support as was described by Adem[11].

pH determinations were done with two potentiometers, a Photovolt (model 111) and a Beckman (model expandomatic) with a precission of ± 0.05 and 0.01 pH units respectively.

1. Electrons

Figure 6 shows the relation between the pH of the solutions and dose, in which it is possible to appreciate a constant change of the pH in the dose range studied. This change is due mainly to the production of HCl formed radiolytically.

The variation of the pH with the concentration is shown in figure 7. These data can be explained from the experimental results of Platford[4], who performed experiments with $^{90}Sr-^{90}Y$ beta radiation and observed that the G(HCl) value increases considerably with the molar concentration of the solutions. These results were plotted in figure 7 for comparation with ours.

2. *X-rays*

Dosimetry was made using the relation (14) and considering $G(Fe^{3+}) = 14.97$. This value was obtained from a graphic combination of the variation of $G(Fe^{3+})$ with energy and also by making use of the X-ray spectrum in the 0-1.0 MeV range. The value of $\overline{(\mu/\rho)}_s/\overline{(\mu/\rho)}_d$ for different concentrations are shown in Table III. The X-ray energy spectrum was obtained from experimental data after Edelsack[18] and plotted in figure 8.

Figure 9 shows that the pH of the irradiated solutions at different concentrations about 0.2 M varies linearly with absorbed dose in the 100 to 700 rads dose range.

3. *Gamma radiation*

Dosimetry was determined with relation (15) using the Fricke method[12] to measure D_d and calculating the values of the fraction $\overline{(Z/A)}_s/\overline{(Z/A)}_d$ for different concentrations. (Table III).

The result of the irradiation can be observed in figure 6, where the response of the solution for high doses is less than in the case of electron irradiations, due to the difference in dose rate, 9.28 Krad/min for gammas and from 0.159 to 1.44 Mrad/min for electrons.

Aqueous solutions of Chloral hydrate can be used for low level dosimetry at different concentrations, with good accuracy due to the precission in the pH measurements and also because there is no difficulty in the solution preparations.

It is found that the expression

$$D = \frac{(pH)_0 - (pH)_i}{4.45} \times 10^4 \text{ (rads)} \qquad (18)$$

can be used as a dosimetric relation for concentrations between 0.2 and 1.0 M, where $(pH)_0$ and $(pH)_i$ are the pH of the original and irradiated solution respectively. For $(pH)_0$ value outside this range, the dose can be read directly from the graph by drawing a curve parallel to the nearest calibration curve, starting from the pH value of the original solution. By this method the indetermination of the measure of the dose is 5% between 200 and 600 rads and about 10% out of this range. The dashed lines in figure 9 may be helpful in drawing these auxiliarly lines. In the same figure it can be observed for concentrations less than 0.05 M the variation of the pH of the irradiated solution decreases rapidly for doses less than 100 rads. In order to better establish this variation, several 0.05, 0.005 and 0.001 M concentrations were irradiated with X-rays, determining the pH variation in situ. The pH meter electrodes were placed in the sample container and reading taking directly by use of a Honeywell Electronic 15 recorder (0 - 2.2 mV range). The results are shown in figure 10 where the voltage variation has been converted to pH variation. The peaks at low doses, less than 15 rads, are due to the unstability of the electrodes current when the radiation beam is on. The recorded data for 0.005 M solution may be used as a dosimetric relation between 10 to 100 rads with a precission about 1 to 2%. This result is particularly useful for Radiation Biology research. Graphs for 0.05 and 0.001 M solutions can be also used for dosimetry with an indetermination about 5% due to the fact that the pH variation is less than in the case of 0.005 M solution. In conclusion, the dosimetric relations found in this paper are useful for determining the amount of radiation energy absorbed in biological systems when subject to X, gamma and electron irradiations.

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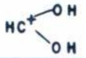
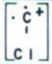
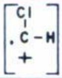
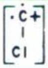
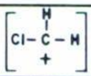
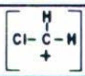
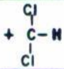
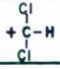
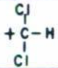
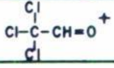
MASS	ION	NON-IRRADIATED (%)	IRRADIATED (%)
18	$[H_2O]^{+}$	5.8	0.7
29	$CH\equiv O^{+}$	55.1	13.5
35	Cl^{+}	11.6	6.9
37	Cl^{+}	3.6	2.1
47	 $HC^{+}\begin{smallmatrix}OH\\OH\end{smallmatrix}$ o  $\left[\underset{Cl}{\cdot\dot{C}^{+}}\right]$	50.0	31.3
48	 $\left[\cdot\overset{Cl}{\underset{+}{C}}-H\right]$	21.2	14.2
49	 $\left[\underset{Cl}{\cdot\dot{C}^{+}}\right]$ o  $\left[Cl-\overset{H}{\underset{+}{C}}-H\right]$	24.1	17.1
50	 $\left[\cdot\overset{Cl}{\underset{+}{C}}-H\right]$	6.9	5.1
51	 $\left[Cl-\overset{H}{\underset{+}{C}}-H\right]$	2.9	2.5
82	$[Cl-\dot{C}-Cl]^{+}$	100.0	100.0
83	 $+\overset{Cl}{\underset{Cl}{C}}-H$	33.9	36.1
84	$[Cl-\dot{C}-Cl]^{+}$	65.6	68.9
85	 $+\overset{Cl}{\underset{Cl}{C}}-H$	21.1	22.9
86	$[Cl-\dot{C}-Cl]^{+}$	12.4	13.8
87	 $+\overset{Cl}{\underset{Cl}{C}}-H$	3.2	4.0
111	 $Cl-\overset{Cl}{\underset{+}{C}}-CH=O \longleftrightarrow H-\overset{Cl}{\underset{Cl}{C}}-C\equiv O^{+}$	31.3	39.7
113	idem	19.7	25.5
115	idem	2.9	4.3
146	 $Cl-\overset{Cl}{\underset{Cl}{C}}-CH=O^{+}$	2.9	5.8
148	idem	2.9	5.8
150	idem	1.0	1.8
152	idem	0.3	0.2

Table I. Relative abundance of the ions detected with mass spectrometry for non-irradiated and irradiated samples of Chloral hydrate, using the Hitachi Perkin-Elmer RMU-6D Mass spectrometer. Relative abundance is shown with respect to mass 82.

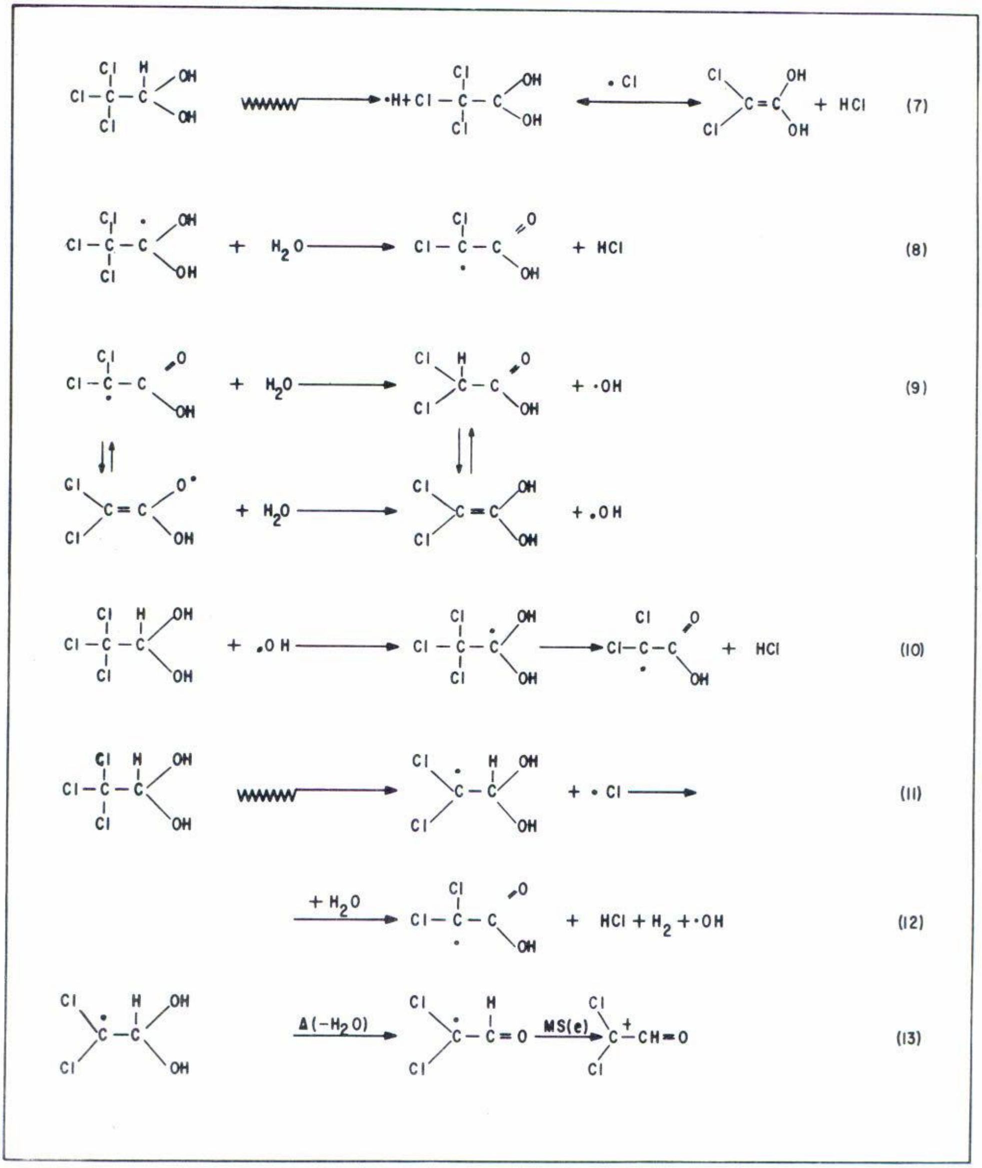


Table II. Collection of reactions of the irradiated Chloral hydrate powder and the radicals formed radiolytically.

Molar concentration (M)	$\frac{\overline{(\mu/\rho)_s}}{\overline{(\mu/\rho)_d}}$	$\frac{\overline{(Z/A)_s}}{\overline{(Z/A)_d}}$
1.0	0.8731	0.9869
0.9	0.8832	0.9887
0.8	0.8918	0.9905
0.7	0.9011	0.9920
0.6	0.9105	0.9940
0.5	0.9198	0.9960
0.4	0.9284	0.9960
0.3	0.9385	0.9989
0.2	0.9470	1.0000
0.1	0.9501	1.0000
0.05	0.9579	1.0000
0.01	0.9642	1.0000
0.005	0.9649	1.0000

Table III. Calculated values for the mean mass energy absorption coefficients and electron densities relations for several molar concentrations.

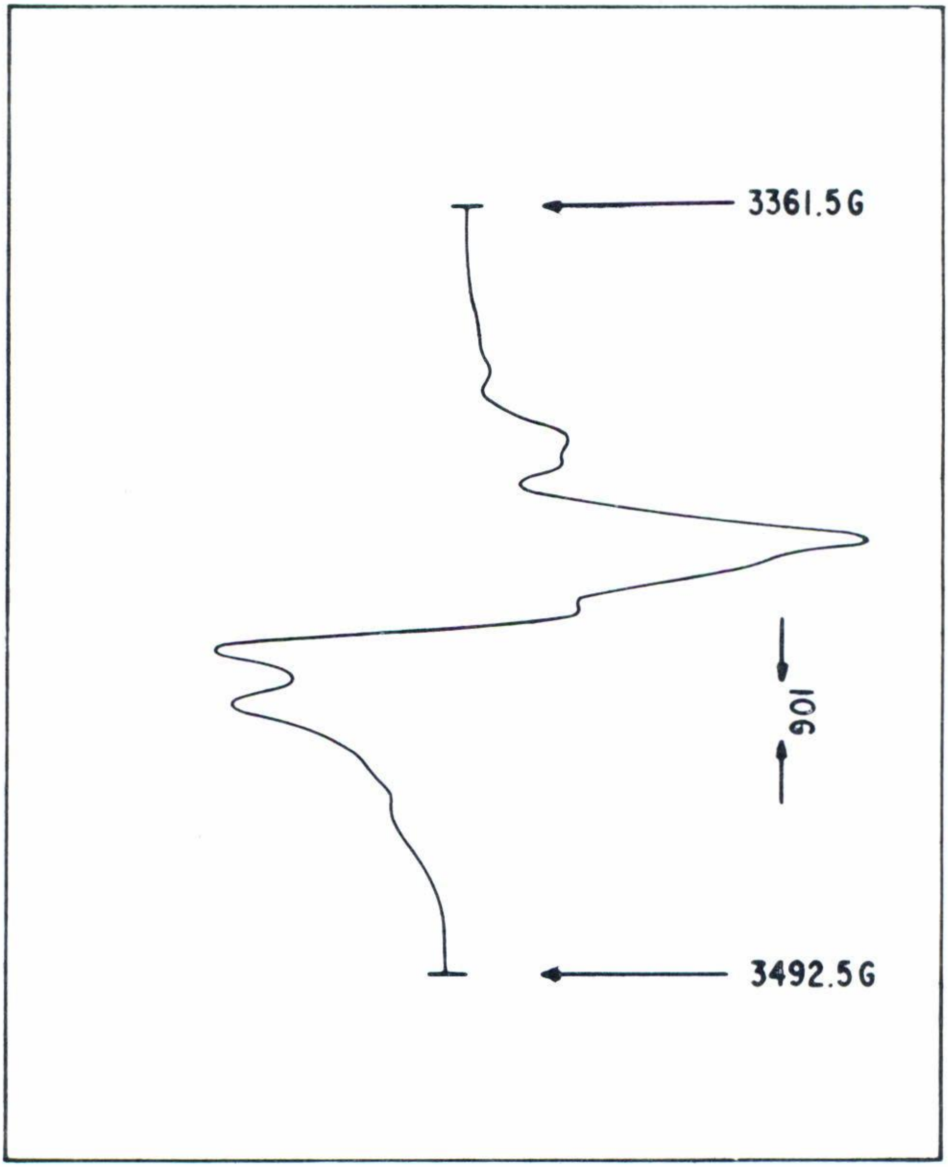


Fig. 1. Typical ESR spectra of electron irradiated polycrystalline Chloral hydrate in air at room temperature to 40 Krads. Values of the field are shown in gauss (G).

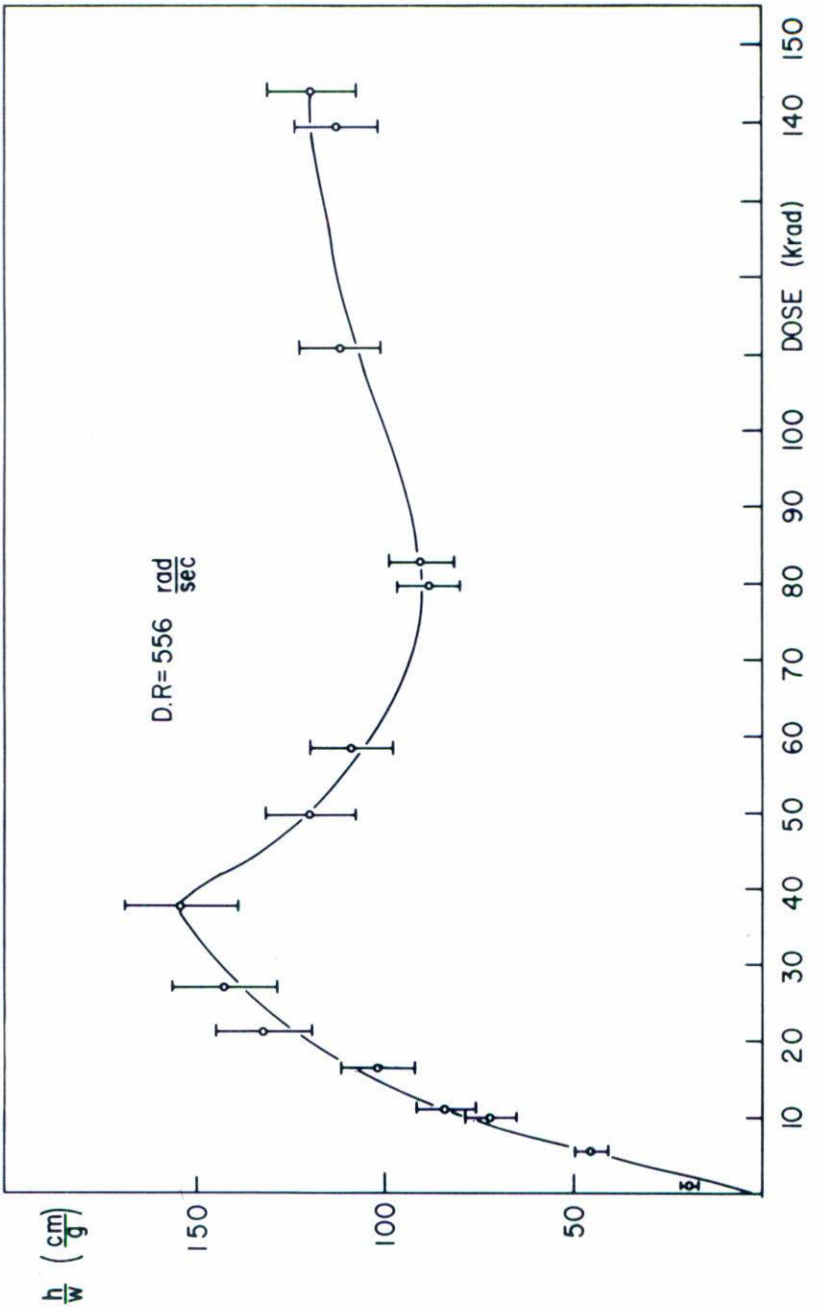


Fig. 2. Production curve of paramagnetic species at different doses in electron irradiated polycrystalline Chloral hydrate in air at room temperature. h/w represents the peak to **peak height** of the first derivative of the resonance signal per mass unit. **D.R. re**presents the dose rate.

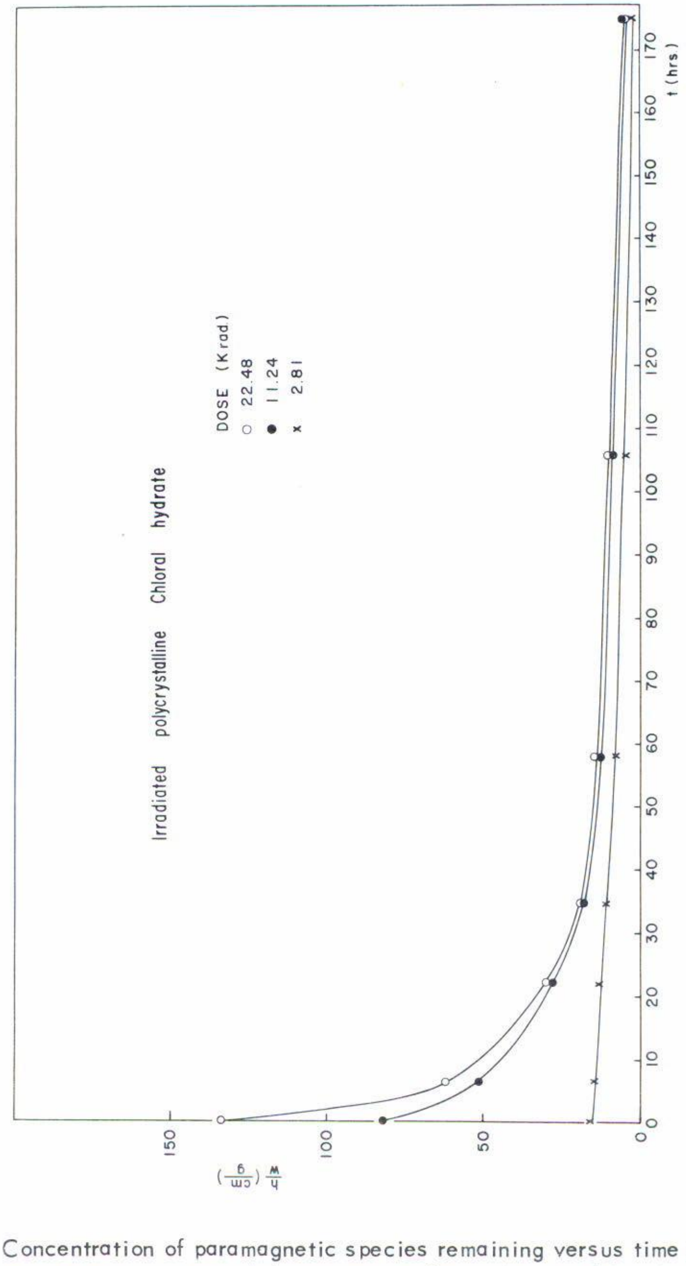


Fig. 3. Concentration of paramagnetic species remaining versus time of storage at room temperature. h/w represents the peak to peak height of the first derivative of resonance signal per mass unit.

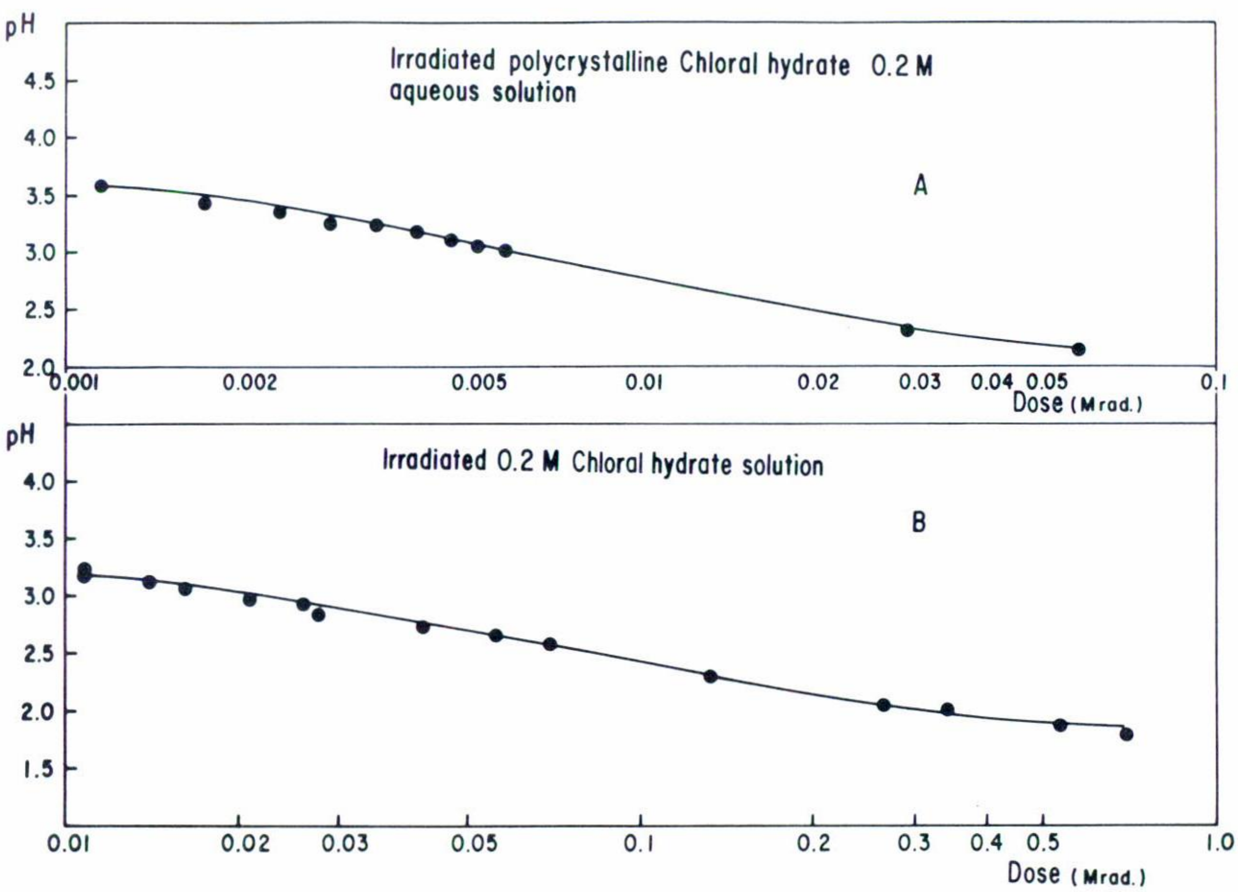


Fig. 4. pH variation of the solutions with dose. Curve A corresponds to the 0.2 M solution prepared with irradiated Chloral hydrate powder. Curve B to the irradiated 0.2 M solution.

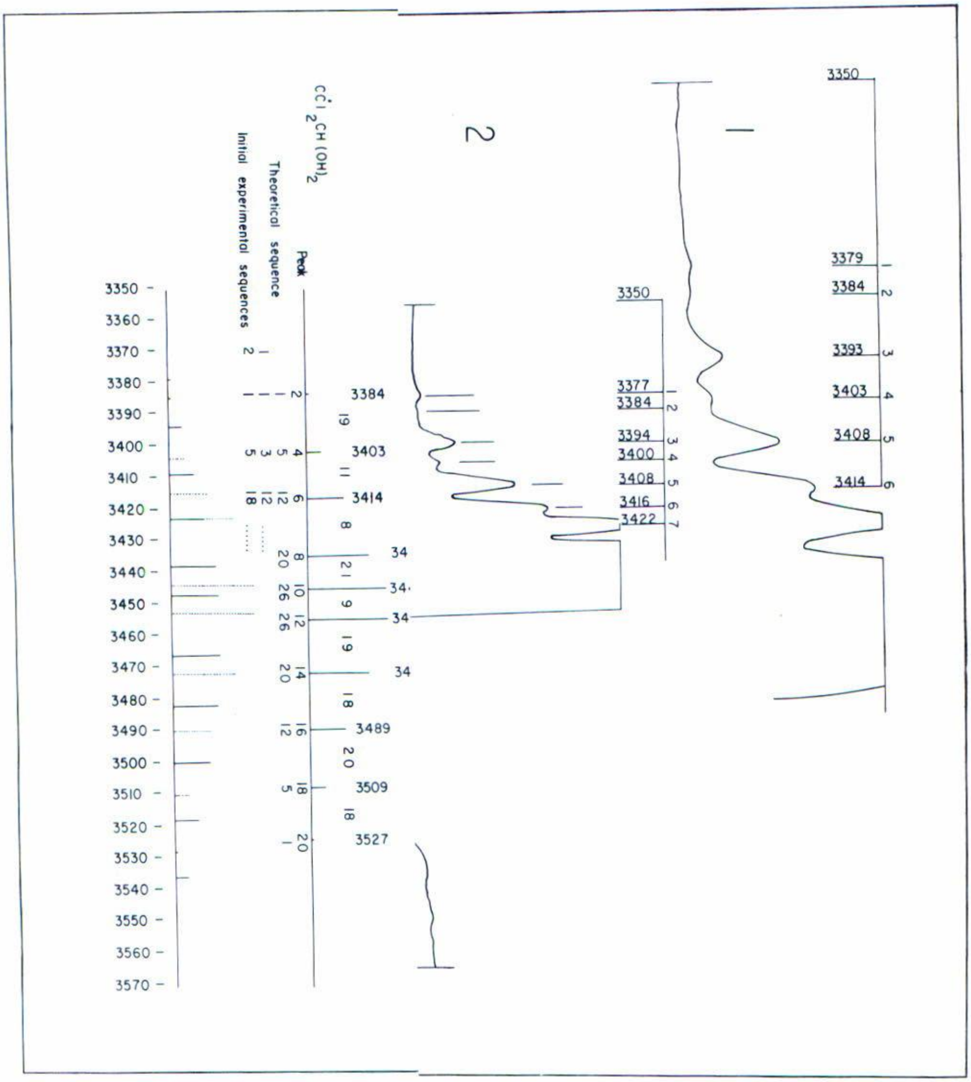


Fig. 5. ESRrating at a microwave frequency in ththe initial experimental relative intetals.

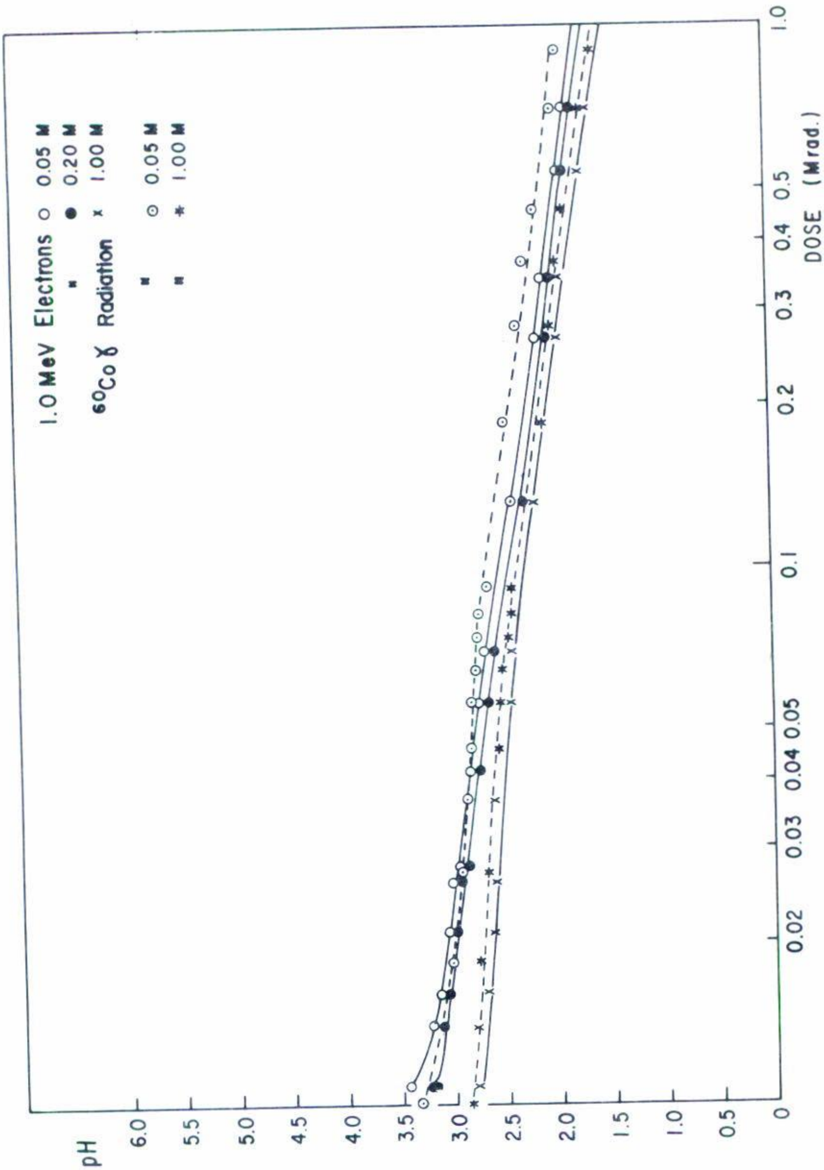


Fig. 6. pH variation of the ^{60}Co gamma and electron irradiated solutions. This variation is due mainly to the production of HCl formed radiolytically.

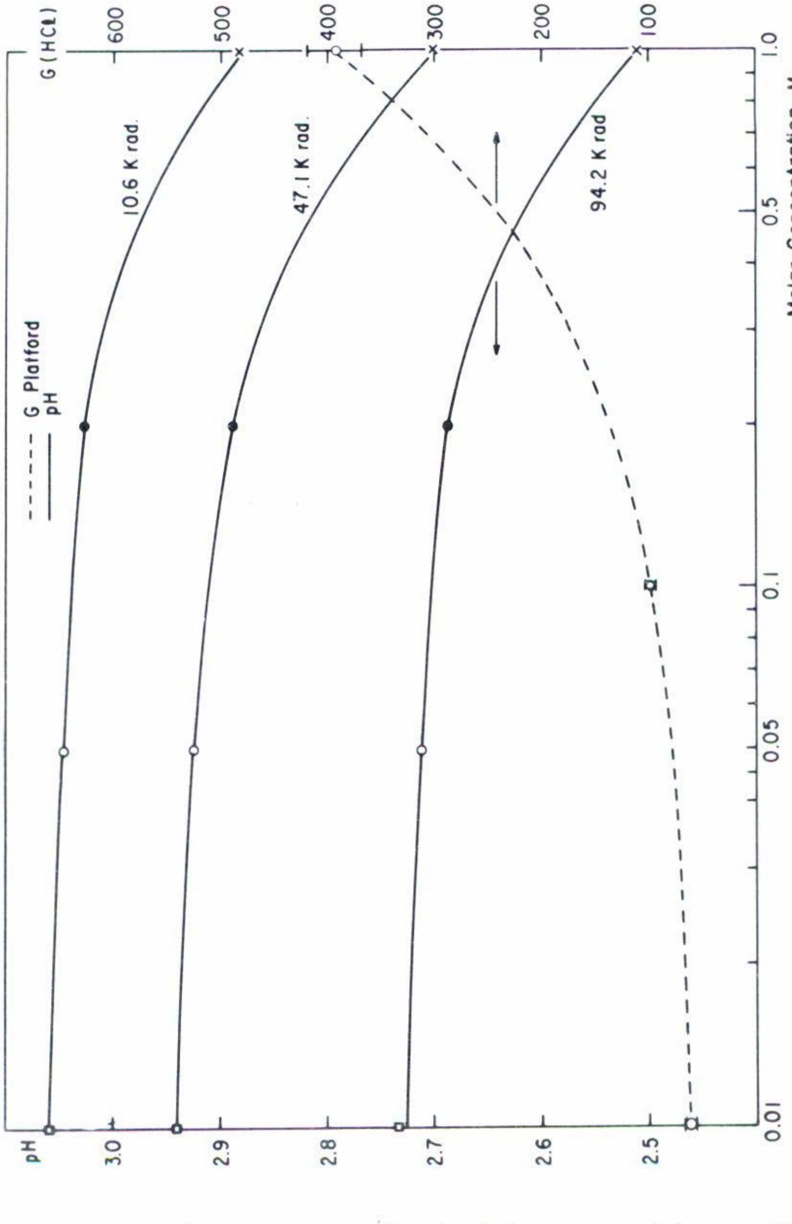


Fig. 7. pH variation of the electron irradiated solution at several doses. The variation of G (HCl) found by Platford[4] explains our result and it is plotted for comparation.

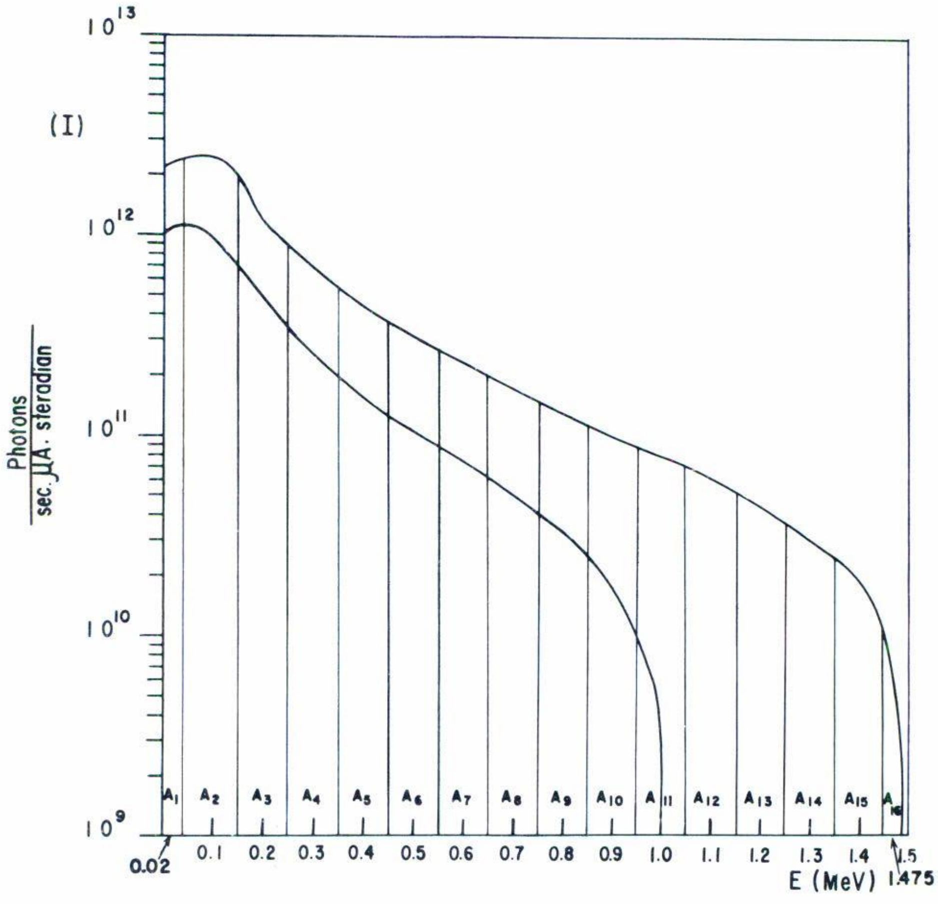


Fig. 8. Bremsstrahlung spectra for 1.0 and 1.5 MeV electrons on a gold target, after Edelsack. (I) represents the intensity of the X-ray beam in photons/sec μA steradian and was measured as was described by Edelsack[18].

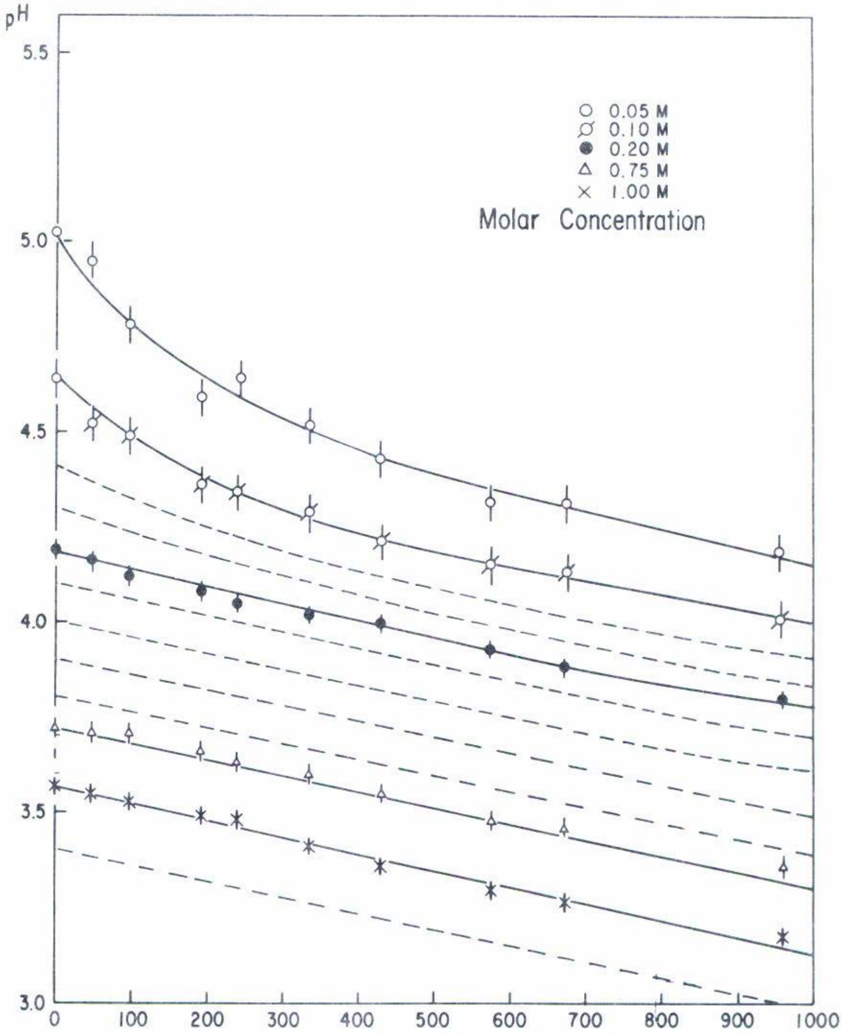


Fig. 9. pH variation of the X-ray irradiated solutions. This relation can be used as a dosimetric relation.

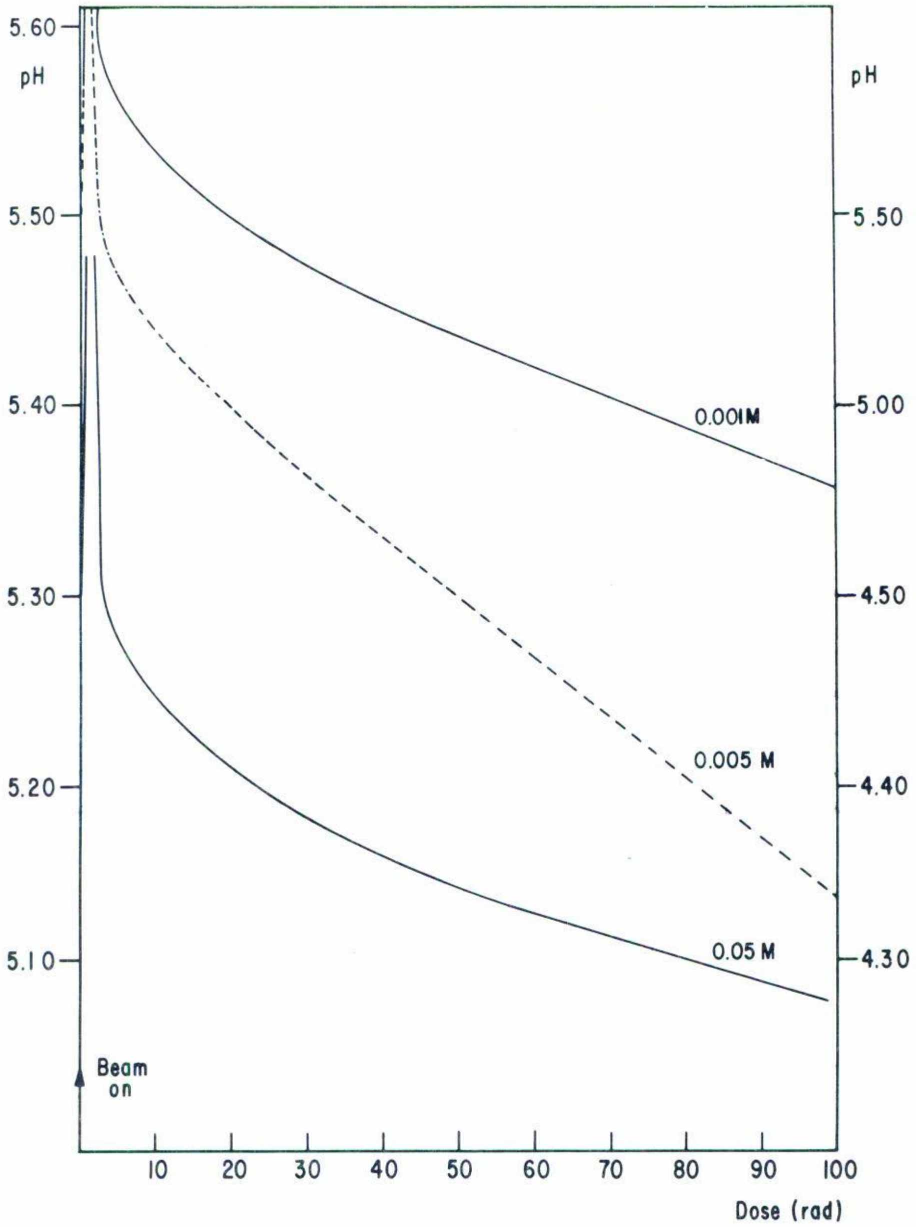


Fig. 10. Dose converted recorded pH variation with X-ray irradiation of Chloral hydrate solutions. Molar concentrations are shown in the figure. The peaks at low doses are due to the unstability of the electrodes current when the radiation beam is on.