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Solid-State Chemistry of Irradiated Choline Chloride[1,2]

Yaffa Tomkiewicz, Ramesh Agarwal, and Richard M. Lemmon

Contribution from the Laboratory of Chemical Biodynamics, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720. Received

Abstract: Further details have been established concerning the radiolysis of the α form of crystalline choline chloride. Esr studies at -196° indicate the presence of a biradical, $(CH_3)_3\overset{+}{N}\cdot\cdot CH_2CH_2OH\text{---}Cl^-$, that diffuses apart with rising temperature, and also indicate the presence of an ethanol monoradical. Radical-decay kinetics, radiolysis kinetics, thermoluminescence studies, and experiments with a photoelectron emitting dye all appear to confirm an important role for detrapped electrons in the radiolysis mechanism.

Crystalline choline chloride, $[(CH_3)_3NCH_2CH_2OH]^+Cl^-$, is the most ionizing-radiation sensitive compound known. Among the most pertinent facts known at the outset of the present study are that (1) the G for radical production (radicals produced/100 eV absorbed) is about 2, while the G for radiolysis (molecules of choline chloride destroyed/100 eV) can be as high as 55,000,[3] (2) a high-temperature polymorph (called the "β" form) is not abnormally radiation sensitive, (3) the main radiolysis products are trimethylamine hydrochloride and acetaldehyde, (4) radiation damage can be deferred indefinitely by irradiating and storing at -78°, and (5) electron donors accelerate the radiolysis, and electron acceptors retard it. The known details of the radiolysis have led to proposals for the radiolysis mechanism,[3,4] but we are still unable to establish the unique property of the choline chloride's α-form (the polymorph that is so radiation sensitive) that makes possible its remarkably efficient chain decomposition.

The present study was undertaken to determine the effect of certain variables on the radical-decay kinetics and radiolysis kinetics of the γ-irradiated α form. The variables employed were total dose, concentration of free electrons, and the temperature at which the radiolysis is allowed to proceed. Because radiolysis does not proceed at low temperatures, we have the opportunity to study the relationship of the radicals created in the α form by the ionizing radiation and those subsequently participating in the chain mechanism of radiolysis. Most of the research reported here was designed to test our previously stated hypotheses that detrapped electrons react with radicals to form excited species that participate in self-propagating chains.[4]

Experimental Section

Our sources of choline chloride and Brilliant Green, purification procedures, method to determine extent of radiolysis, source of γ rays, irradiation techniques, and general laboratory procedures were recently described.[3] The electron spin resonance spectra, and changes of radical concentrations, were determined on a Varian Model E-3 spectrometer equipped with a variable temperature assembly. Thermal emission characteristics were observed with a Harshaw Model 2000A thermoluminescence detector, to which we added an external temperature programmer. All thermoluminescence experiments were done with a temperature rise rate of 20°/minute.

Results and Discussion

Esr Spectra. Figure 1 shows the esr spectrum of a polycrystalline sample of choline chloride γ-irradiated at -196° and measured at the same temperature. Figure 2 shows the corresponding spectrum of an identical sample that was also irradiated at -196°; it was then warmed to -20°, then recooled to -196°. It is obvious that some irreversible changes occur during the warming. These changes have been observed by Symons[5] who interpreted them as reflecting the disappearance of $ClOH^-$ radicals. However, we believe that they are more likely explained by the diffusing apart of spin-coupled radicals and by a change in the nature of the monoradicals (see below). In addition, the formation of $ClOH^-$ would depend upon the presence of water--and we have found unchanged esr spectra regardless of whether our deliquescent crystals were exposed to air or to conditions of rigorous moisture exclusion.

In Figure 3 we have recorded the esr spectrum (at -166°) of a γ-irradiated polycrystalline sample in the magnetic-field range

corresponding to microwave power absorption by biradicals. Here, the signal corresponds to a simultaneous flip of two electron spins on different radicals coupled by a spin-spin interaction ($\Delta M_S=2$).[6] The two most plausible explanations for this biradical interaction appear to be (1) "pairwise trapping" of the two radicals formed from the choline chloride molecule, as indicated by the previously given formula,[3] $(CH_3)_3\overset{+}{N}\cdot\cdot CH_2CH_2OH\cdots Cl^-$, or (2) an inter-radical interaction between two ethanol radicals. (As we have previously reported,[3] our esr spectrum at room temperature corresponds to that of an ethanol radical. No trimethylamine radicals were seen, presumably because of excessive broadening by the nine protons; however, Symons has reported that these radicals are observed in his esr spectra.[5]) We believe that the second explanation is not correct because we have previously searched for, but found no traces of, either 1,4- or 2,3-butanediol as products of the choline chloride radiolysis.[7] It therefore appears that our $\Delta M_S=2$ absorption is by an intra-radical coupling, namely, by a biradical with the formula given above. The existence of such "pairwise trapping" has been frequently reported.[8-13]

In general, the zero-field splitting parameters (D and E)[14] for paramagnetic species is given by:

$$(D^2 + 3E^2)^{1/2} = [3\,\frac{(h\nu)^2}{4} - 3(g\beta H)^2]^{1/2}$$

where $h\nu$ is the energy of the absorbed microwaves, g is the dimensionless proportionality constant between the electron's magnetic moment and angular momentum, β is the Bohr magneton (0.927×10^{-20} erg/gauss), and H is the magnetic field strength. For radical pairs, E is usually assumed to be approximately zero.[15] D is related to R, the inter-radical

distance, by the expression (for random orientation) $D = 3\beta g/2R^3$; for our spectrum at -196° this distance was found to be 6 Å.

The biradical also has an absorption in the $\Delta M_S=1$ (monoradical) region. The ratio of biradical transition probabilities at $\Delta M_S=2$ and $\Delta M_S=1$, respectively, is (also for random orientation):[15]

$$\frac{I_2}{I_1} = \frac{4}{15}\left(\frac{D}{H_o}\right)^2$$

where H_o is the field value for the $\Delta M_S=1$ transition. This ratio was found in our case to be 5×10^{-4}. By performing double integration of the measured $\Delta M_S=1$ and $\Delta M_S=2$ absorption curves one can find the relative weight of the monoradical and biradical $\Delta M_S=1$ transitions. The method is the following: If I_2 is the measured intensity of the biradical at the $\Delta M_S=2$ position, I_1 is the intensity of the biradical at $\Delta M_S=1$ and I_M is the intensity of the monoradical, then the value Q (= intensity of the $\Delta M_S=1$ transition/intensity of the $\Delta M_S=2$ transition) is

$$Q = \frac{I_M + I_1}{I_2} = \frac{I_M + I_2 \frac{15}{4}\left(\frac{H_o}{D}\right)^2}{I_2}$$

For our case, $I_M/I_1 = 4$, meaning that 20% of the measured intensity at the $\Delta M_S=1$ transition can be attributed to the biradical. There is a possibility that the marked peaks in Figure 1 belong to the biradical, since the separation between them fits the calculated zero-field splitting parameter of 140 gauss.[15]

Temperature effects were also observed in the $\Delta M_S=1$ and $\Delta M_S=2$ transitions. An irradiated (-196°) sample was warmed at a given temperature for approximately 10 min, recooled to -166° (the lowest temperature

attainable in the variable-temperature unit), and the spectrum recorded. The same sample was then warmed to another annealing temperature (10 min) and again recooled to -166° for another observation of the esr spectrum. This method eliminated influences of such reversible temperature effects as motional narrowing and magnetic susceptibility.

In Figure 4, curves a and b give the peak-to-peak heights of the $\Delta M_S=1$ and $\Delta M_S=2$ transitions, respectively, as a function of the annealing temperature. The signals are decaying simultaneously up to about -110°. However, at higher temperatures the biradical signal continues to show considerable decay while the monoradical signal stays nearly constant. The fact that the $\Delta M_S=1$ transition stays practically constant for annealing temperatures higher than -110° indicates that the change in the region from -130° to -110° is probably not due to a crystalline phase transition; if it were we would expect successive losses in radical signal each time we passed through that temperature range. It therefore appears plausible to relate the $\Delta M_S=1$ change above -130° to a change in the nature of the monoradical. Comparison of Figs. 1 and 2 clearly shows the change in the radical spectrum upon warming (the spectrum of Fig. 2 is very similar if the sample is warmed only to -110°). However, the change is gradual from -196° to -110°.

We visualize the radical formation as follows: The ionizing radiation creates at -196° a "precursor" monoradical. It is stable up to -130° but could not be identified because of its broad spectrum, and because that spectrum overlaps the biradical $\Delta M_S=1$ transition. In the -130° to -110° range the precursor radical is transformed into another monoradical (the change may be only conformational) that is stable up to temperatures

where its hyperfine is resolved. This radical was identified as the ethanol radical. The corresponding decrease in the biradical signal as one goes through the -130° to -110° region (see Fig. 4) is also presumed to be related to the monoradical's transformation.

The explanation for the continued decrease in the biradical's signal above -110° can be that the two monoradicals (one, the ethanol radical discussed above; the other, the trimethylamine radical discussed below) are diffusing away one from each other and, therefore, the interaction between the coupled spins decreases. In order to test the validity of this explanation, the values of D were calculated for different annealing temperatures (after cooling back, of course, to -166°). Within the limit of our accuracy, D was found to decrease (i.e., the inter-radical distance, R, increases) with an increase in the annealing temperature.

We need to comment on our failure to observe the other monoradical, which would be a trimethylamine precursor. This failure may be due to excessive broadening by the nine protons. It may also be due to a low transitional probability for that particular radical. In addition, this monoradical may disappear by interaction with the electrons that are depopulated between -40° and -10° (see next section).

These esr observations are in accord with the mechanism that was proposed earlier[4] to account for the radical formation in irradiated choline chloride: The radiation excites the molecule, leading to a partial homolysis of the nitrogen-to-methylene bond. The biradical's subsequent fission seems to be apparent in our temperature studies. However, the biradical (but not the monoradical) esr signal completely disappears before the chain propagation begins (see below), and there is, therefore,

no apparent connection between the biradical formation and the choline chloride's unusual radiation sensitivity.

Thermal Emission of γ-Irradiated Choline Chloride Crystals. Irradiation of many crystals liberates electrons, some of which become localized in traps. As soon as a high enough temperature is reached, these electrons will be released. They can move in the conduction band and combine with trapped holes, a process that may result in photon emission. With increasing temperature, the emission will rise to a peak and then decay as the traps are emptied. We have found this thermal emission for γ-irradiated choline chloride crystals. Two pre-existing (before the irradiation) traps were identified: From one of them the electrons are released between -40° and -10°.[16] The other trap has a peak emission at about 67°; this corresponds to an energy depth of 2 ± 0.2.[17]

Figure 5 shows the thermal emission characteristics of samples irradiated for 1.25 megarads (curve a) and 15 megarads (curve b). The higher-dose sample has, in addition to the discrete trap sets, a continuous luminescence reflecting a broad spectrum of trap depths.

An attempt was made to determine the spectral range of the measured thermal emission. The determination was not very accurate since the photomultiplier currents which are involved were of the order of 10^{-12} amp. By using a Kodak Wratten A-2 filter we estimated that the thermal emission peaks were above 410 nm. This indicates that the emitting state is not singlet since we have observed that the absorption spectrum of choline chloride has no peak above 200 nm. Most probably it is a triplet since, according to Brocklehurst,[18] hole-electron recombination gives triplet to singlet in the approximate ratio of 3:1 consistent with multiplicity.

The Effect of Free Electrons on the Radiolysis Process. In previous work, Brilliant Green (a photoelectron-emitting triphenylmethane dye[19]) was found to enhance the radiolysis.[3] The technique was to add the finely-divided dye to γ-irradiated, finely-divided choline chloride, and then to illuminate the mixture. Because strong illumination (a G.E. A-H6, high-pressure mercury arc) was used, it was possible that heat, rather than photoelectrons, caused the increased radiolysis. However, exposure of finely-divided mixtures of γ-irradiated choline chloride-non-γ-irradiated Brilliant Green (1:1 by weight) to different rates of A-H6 illuminations (same total number of photons) gave the same amounts of radiolysis. Evidently, heat plays no role in the Brilliant-Green enhanced radiolysis. In the absence of the dye the origin of the free electrons is probably thermally-depopulating traps.

From our thermoluminescence results we conclude that the shallow traps are at least as populated as the deep traps. However, the radiolysis is negligible in the temperature range where the shallow traps are depopulated.[4] A very possible explanation is that at these low temperatures, radical-electron interactions are much less probable than hole-electron interactions. But if this is the case, by releasing the electrons from the shallow traps at high enough temperatures, one can enable them to participate in the radiolysis process. Again, from thermoluminescence data we know that sudden (about 15 sec) heating of a sample from -80° to 50° releases electrons from the shallow traps even at 50°, while slow heating already depopulates the shallow traps at about 0°. Therefore, we gave different thermal treatments to two samples of γ-irradiated choline chloride. One sample was warmed from liquid nitrogen temperature to 0°,

kept at this temperature for 15 min, then warmed up to 50° and kept at this temperature for 15 min. The second sample was warmed up suddenly from liquid nitrogen to 50°. In the first case the shallow traps will depopulate before the radiolysis can take place, while in the second case they could participate in the radiolysis. We found the results of the radiolyses to be identical for both samples. It is therefore evident that electrons from the shallow traps are not participating in the radiolysis.

The Effect of Free Electrons on the Radical Decay. A γ-irradiated sample was mixed with Brilliant Green (1:1 by weight). The mixture was placed in the esr cavity and the ethanol radical decay kinetics were investigated as a function of illumination in the visible region (Corning 3-69 and 1-69 filters) of a 450-watt xenon arc. In both the illuminated and non-illuminated samples the temperature was maintained at 12°. With the lamp at a distance of 15 cm from the sample (as close to the cavity as possible, and with optimal focussing) the illumination increased the radical-decay rate by a factor of 2.5. We attribute the enhanced radical decay in the presence of the illuminated Brilliant Green to reaction of the radicals with the electrons donated by the dye.

Additional evidence was obtained for the participation of electrons in the radical decay. We studied the ethanol radical decay kinetics for two samples--one was irradiated with 1.25 megarads and the second was irradiated with 15 megarads. The decay of the radical signal in the sample irradiated with the higher dose was found to be faster than the decay in the sample irradiated with the lower dose, even after the concentration of the radicals at the "higher dose", was lower than the

concentration of the radicals at the "lower dose". Simultaneous studies of the thermal emissions of the samples irradiated with 15- and 1.2- megarad doses showed that the free-electron concentration is greater in the higher-dose sample than in the lower-dose sample, even after the concentrations of the radicals become equal in both of the samples. Therefore, it seems plausible that the enhanced radical decay in the high-dose sample, even after the "crossing point" of radical concentrations, is due to the excess of free electrons in that sample.

We also observed the temperature dependence of the ethanol radical kinetics. The radical decay was found to be extremely slow, as is the radiolysis, for temperatures below 10°. Since we know from thermal emission data that electrons are released below 10° it appears (as surmised above) that the radicals are not reacting with them because radical-electron interactions are less probable at the low temperatures than hole-electron interactions. Another explanation for the lack of reaction with the ethanol radicals would be a preferential reaction with the trimethylamine radicals.

The ethanol radical decay does not fit either first- or second-order kinetics. However, all features of these kinetics can be explained on the basis of electron-radical interactions. The decrease of the slope of the logarithm of the radical concentration as a function of time (at a given temperature) can be explained by a decrease of the free electron concentration due to a lowering of the population in traps. The higher initial slope, and its more pronounced decrease at higher temperatures can also be explained by faster thermal depopulation of the traps.[20]

Influence of the Dose on the Irradiated Samples. In previous work we found that the radical concentration increased almost linearly with

dose up to a total of 23.7 megarads.[4] We performed similar studies with regard to the electron concentration using thermal emission as the tool. We found that the ratio of thermal emissions of samples irradiated with 15 megarads and 1.25 megarads is about 2, while the ratio of the respective radical concentrations is about 12. A possible explanation for this observation is that the number of electrons liberated by the high dose is indeed proportionately higher than the number liberated by the lower dose; however, since the number of the available traps is small, the traps are saturated and the excess of electrons is lost.

Effect of dose and temperature on radiolysis kinetics. One would expect that the amount of radiolysis would increase with dose due to increased production of radicals and trapped electrons. For short times of post-irradiation storage this is true, but for longer times this does not seem to be the case. At room temperature (where the effect is most clear), the radiolysis occurring during 7 days (= 10,080 hr) storage is less for a 15-megarad sample than for a 1.25-megarad sample (Figure 6). At 50° (see Figure 7), the 1.25-megarad sample will probably give a higher final radiolysis than the 5- and 15-megarad samples (the latter have reached the "saturation radiolysis"[3] of about 13-16%, while the 1.25-megarad sample's radiolysis is still increasing). We believe that the explanation for a greater final radiolysis in a sample that received less radiation is the following: In samples that have received as high as 15 megarads we have observed as much as 0.3% radiolysis, even at -196°. Chromatographic analyses of the products formed under these conditions showed that they were not the usual ones (trimethylamine hydrochloride

and acetaldehyde). Such unusual products may be responsible for the diminished radiolysis.

However, as the data of Figure 7 show, the post-irradiation treatment at 71° has brought about an expected faster attainment of the "saturation" radiolysis but at a lower value (around 10%) compared to the usual values of 13-16%. The reason is probably the occurrence of other radical and electron reactions that may not contribute to the radiolysis; examples would be radical-radical interactions (such as dimerization and disproportionation) and the capture of electrons by holes. These processes will have different activation energies, and one or more of them may become more important at a higher temperature (such as 71°). This high-temperature saturation-radiolysis behavior was confirmed by heating samples at five different temperatures between 50° and 75° for 100 min, the time at which all samples should reach saturation radiolysis. The results, which are shown in Table I, show clearly that the radiolysis does indeed decrease with increase in temperature.

It may be of great significance that at 74° the radiolysis has only reached about 9%. In the β-form, the form which is radiation stable and exists at temperatures above 80°, the radiolysis was found to be negligible. We have long suggested that the α and β forms differ in some respect (e.g., distance between key atoms in adjacent choline ions) that account for the differences in radiation sensitivity. The above observations offer another possibility: that at 80° the processes discussed above are so important that the radiolysis does not take place regardless of which crystalline form (α or β) is present.

Table I. Dependence of Choline Chloride Radiolysis on Dose and Post-Irradiation Temperature

Temp. (for 100 min)	Dose (megarad)	% Radiolysis
51°	5	12.6
	10	13.0
63°	5	12.2
	10	12.6
67°	5	12.0
	10	12.1
71°	5	10.2
	10	10.1
74°	5	8.7
	10	9.3

Proposed radiolysis mechanism. The data we now have on radical and free-electron involvement in the radiolysis is consistent with the following mechanism:

(1) $(CH_3)_3\overset{+}{N}CH_2CH_2OH \rightsquigarrow [(CH_3)_3\overset{+}{N}CH_2CH_2OH]^* \longrightarrow (CH_3)_3\overset{+}{N}\cdot\cdot CH_2CH_2OH$

(2) $\cdot CH_2CH_2OH + e^- \longrightarrow [:CH_2CH_2OH^*]^-$

(3) $[:CH_2CH_2OH^*]^- + (CH_3)_3\overset{+}{N}CH_2CH_2OH$

$\downarrow$

$CH_3CHO + (CH_3)_3\overset{+}{N}H + [:CH_2CH_2OH^*]^-$

(4a) $(CH_3)_3\overset{+}{N}\cdot + [:CH_2CH_2OH^*]^- \longrightarrow (CH_3)_3\overset{+}{N}CH_2CH_2OH + e^-$

(4b) $(CH_3)_3\overset{+}{N}\cdot + [:CH_2CH_2OH^*]^- \longrightarrow (CH_3)_3\overset{+}{N}H + CH_3CHO + e^-$

Overall reaction: $(CH_3)_3\overset{+}{N}CH_2CH_2OH \longrightarrow (CH_3)_3\overset{+}{N}H + CH_3CHO$

Reaction (1) shows the formation of the observed biradical from an electronically-excited choline cation (for simplicity the Cl^- ions have been omitted). Reaction (2) indicates the reaction of a detrapped electron with the ethanol monoradical, after or accompanying the diffusing-apart of the biradical. The resultant excited anion would be the chain propagator, as shown in reaction (3). Reactions (4a) and (4b) are both possible termination reactions. The first reforms a choline cation; the second forms the two stable products. Both seem equally possible.

Summary

This work has added to our knowledge of the radicals that appear in γ-irradiated choline chloride, and has added further evidence of the important role of free electrons in the radiolysis mechanism. The irradiated crystalline compound has been shown to exhibit the following characteristics:

1. The changes with temperature of the esr spectra appear to reflect a diffusing apart of an initially-formed $(CH_3)_3\overset{+}{N}\cdot\cdot CH_2CH_2OH\text{---}Cl^-$ biradical. At -196° the distance between the coupled spins is about 6 Å.

2. Thermoluminescence observations have shown the release of trapped electrons from two principal trap depths, and have also shown that higher doses of radiation create larger numbers of trapped electrons in the crystals. The electrons released from the lower temperature (lower energy) trap appear to play no part in the radiolysis.

3. It was confirmed that the photoelectron-emitting dye, Brilliant Green, enhances the radiolysis; it also speeds the rate of radical decay.

4. The radical decay rate is extremely slow below 10°, and, at a given temperature, this rate diminishes with time. The reduced rate

appears to be a result of a diminishing availability of free (detrapped) electrons.

5. The decay of radical signals in high-dose samples can continue to be faster than that in a low-dose sample even after a point of equal radical concentrations is reached. Thermoluminescence observations have shown that, at this "cross-over" point, the higher-dose samples still have available a higher concentration of trapped electrons.

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(2) Presented at the Symposium on Organic Solid State Chemistry, 164th National Meeting of the American Chemical Society, New York, N. Y., Sept. 1972.

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(20) An additional possibility to explain the time dependence of the radical decay rate is that the products (mostly trimethylamine hydrochloride and acetaldehyde) are quenchers for the free electrons. (They are not acting as quenchers for the radicals since, if they were, the radical decay rate would increase with time.)

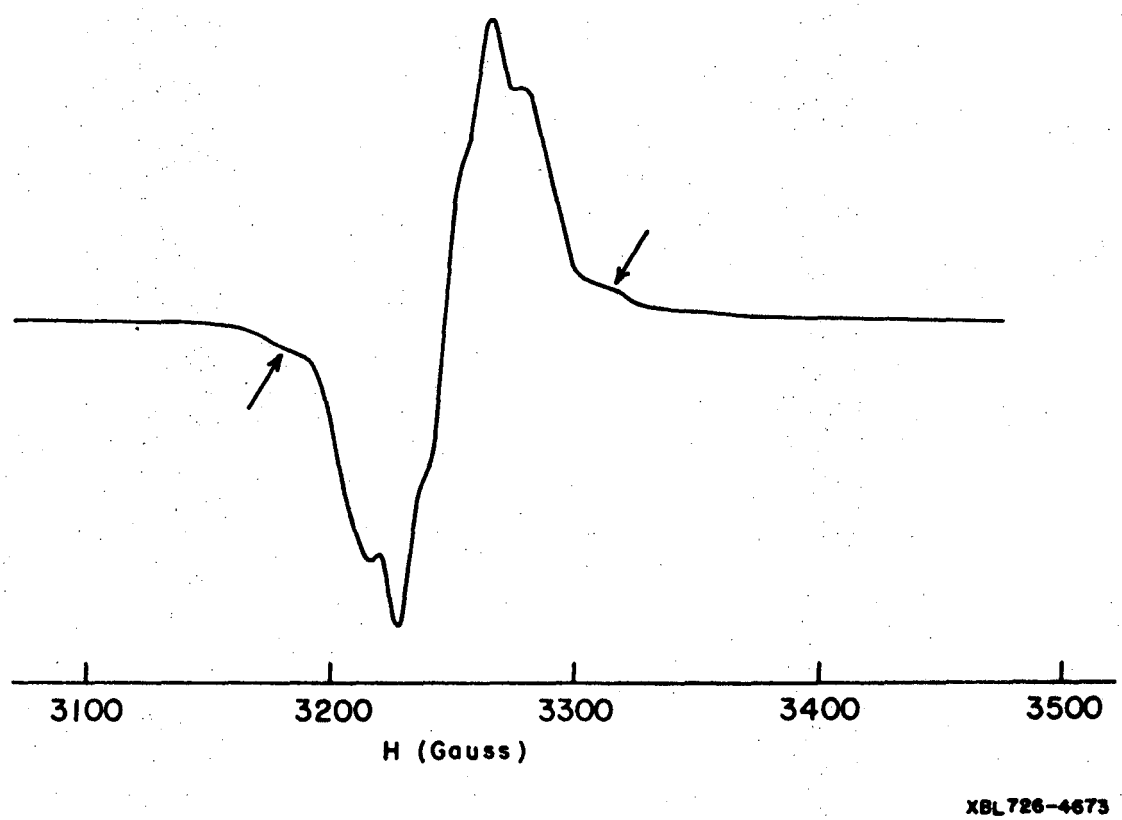

Figure 1. Esr spectrum of polycrystalline choline chloride - irradiated at -196°, spectrum at -196°.

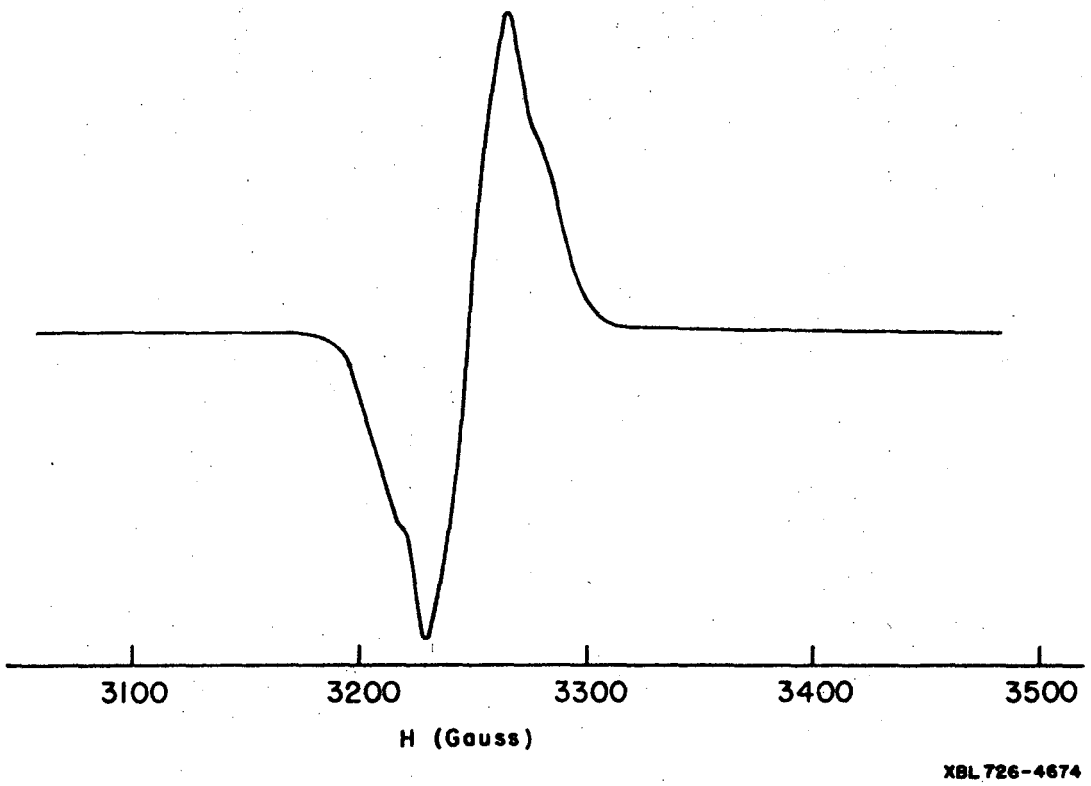

Figure 2. Esr spectrum of polycrystalline choline chloride - irradiated at -196°, warmed to -20°, and spectrum recorded at -196°.

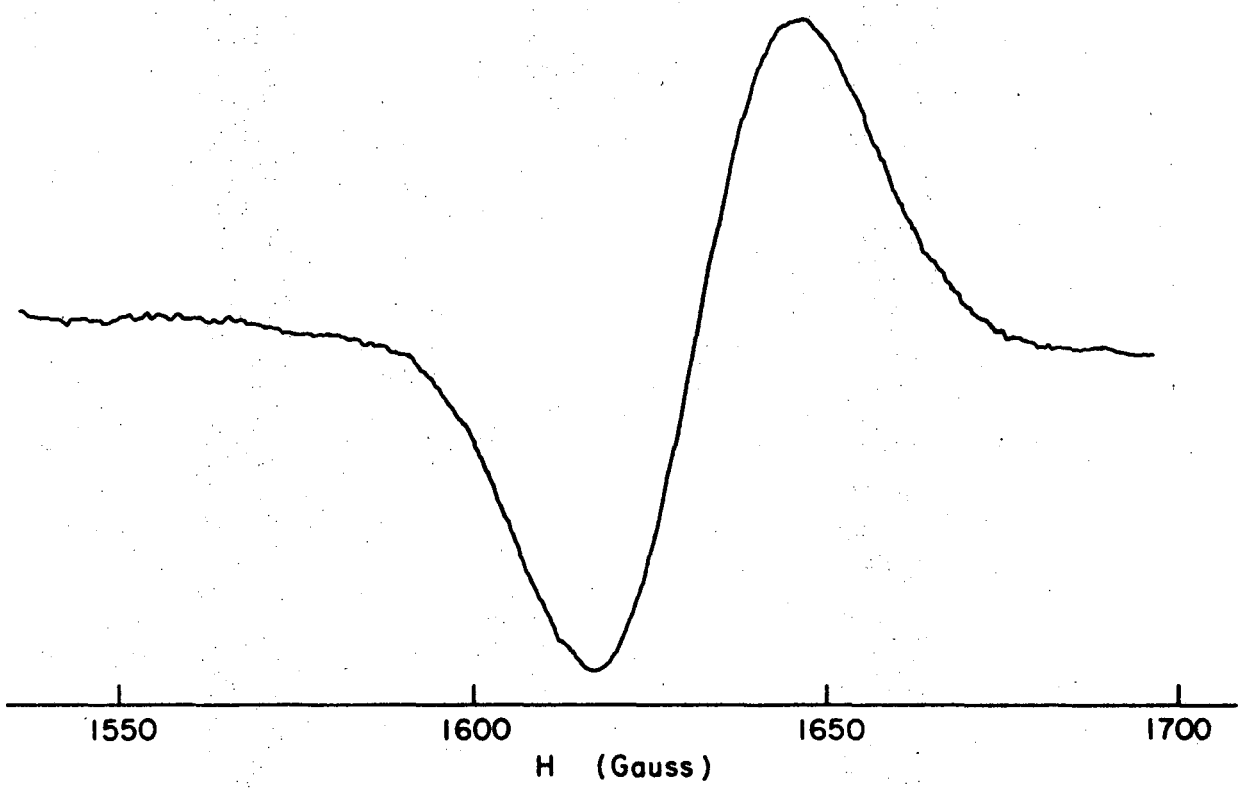

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Figure 3. The biradical esr absorption (at -166°) corresponding to the $\Delta M_S=2$ transition.

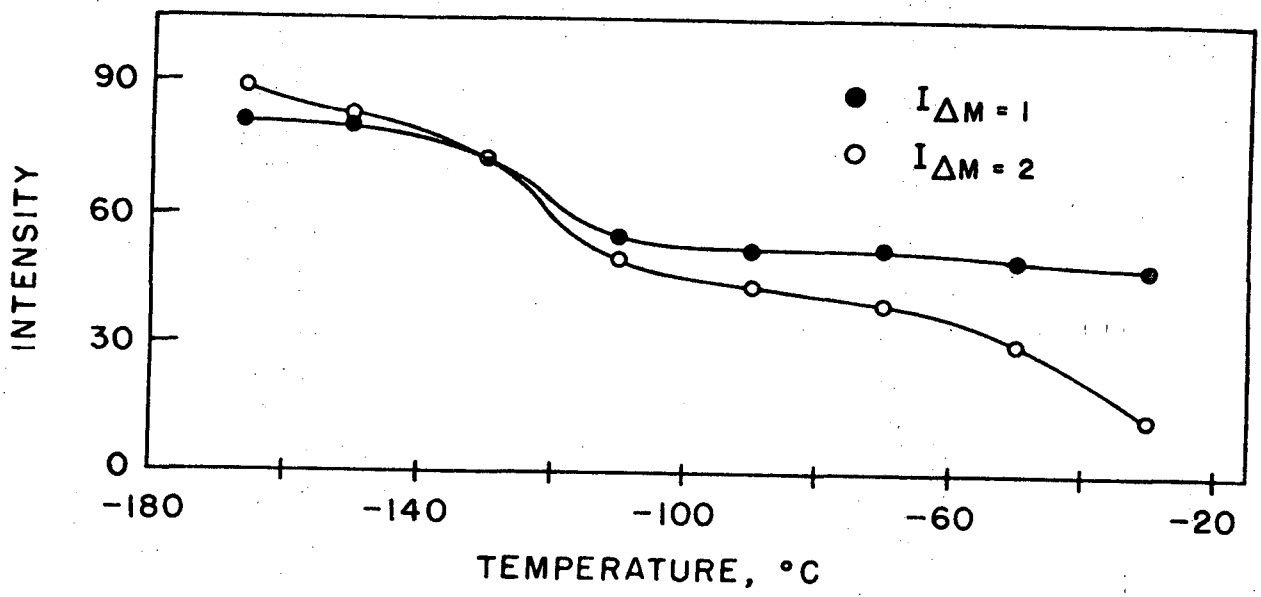

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Figure 4. a) Esr intensity of monoradical at -166° in choline chloride (irradiated at -196°) as a function of annealing temperature. b) Esr intensity of biradical at -166° in choline chloride (irradiated at -196°) as a function of annealing temperature. c) The ratio of intensities of biradical and monoradical in choline chloride (irradiated at -196°) at various temperatures. d) The same ratio at -166° after the sample is recooled from various annealing temperatures.

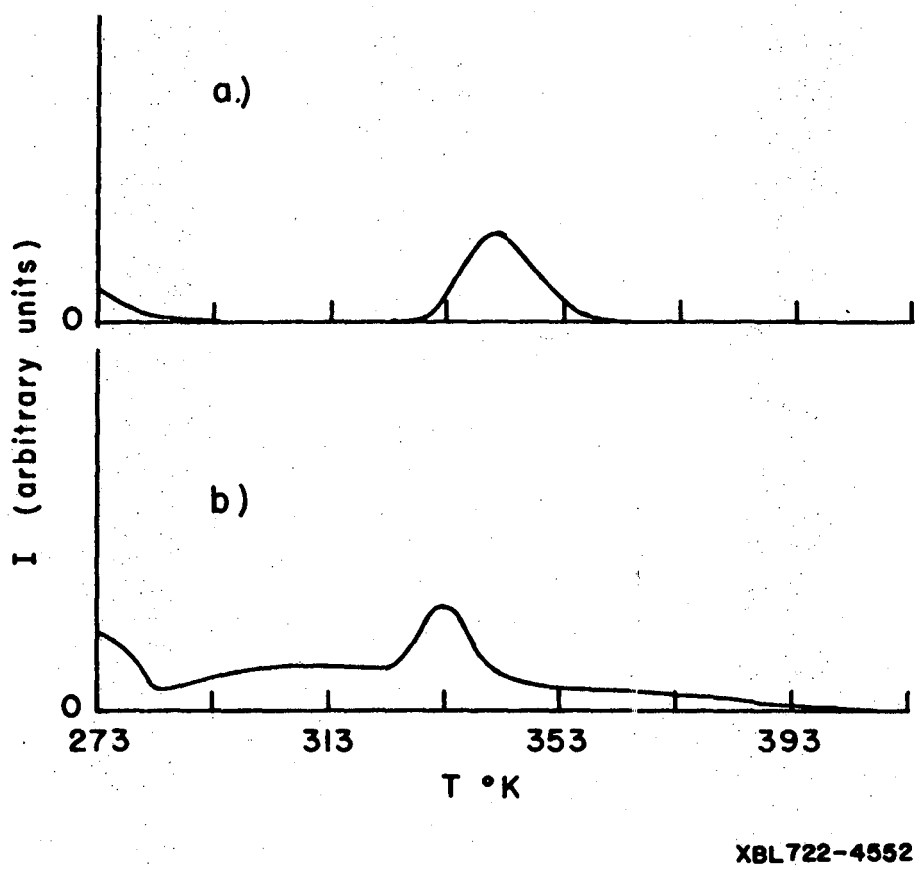

Figure 5. Thermal emission of choline chloride samples irradiated with (a) 1.25 megarads and (b) 15 megarads of γ-rays.

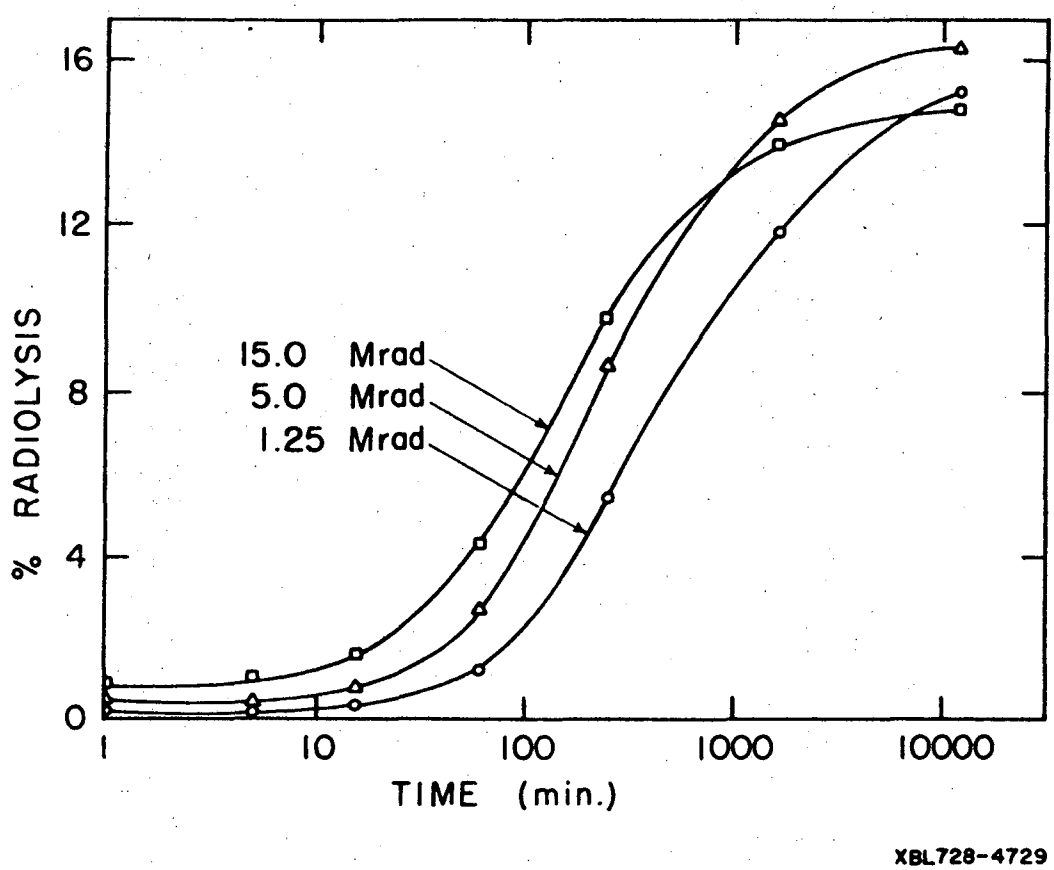

Figure 6. Choline chloride radiolysis kinetics at 22.5° as a function of total radiation dose.

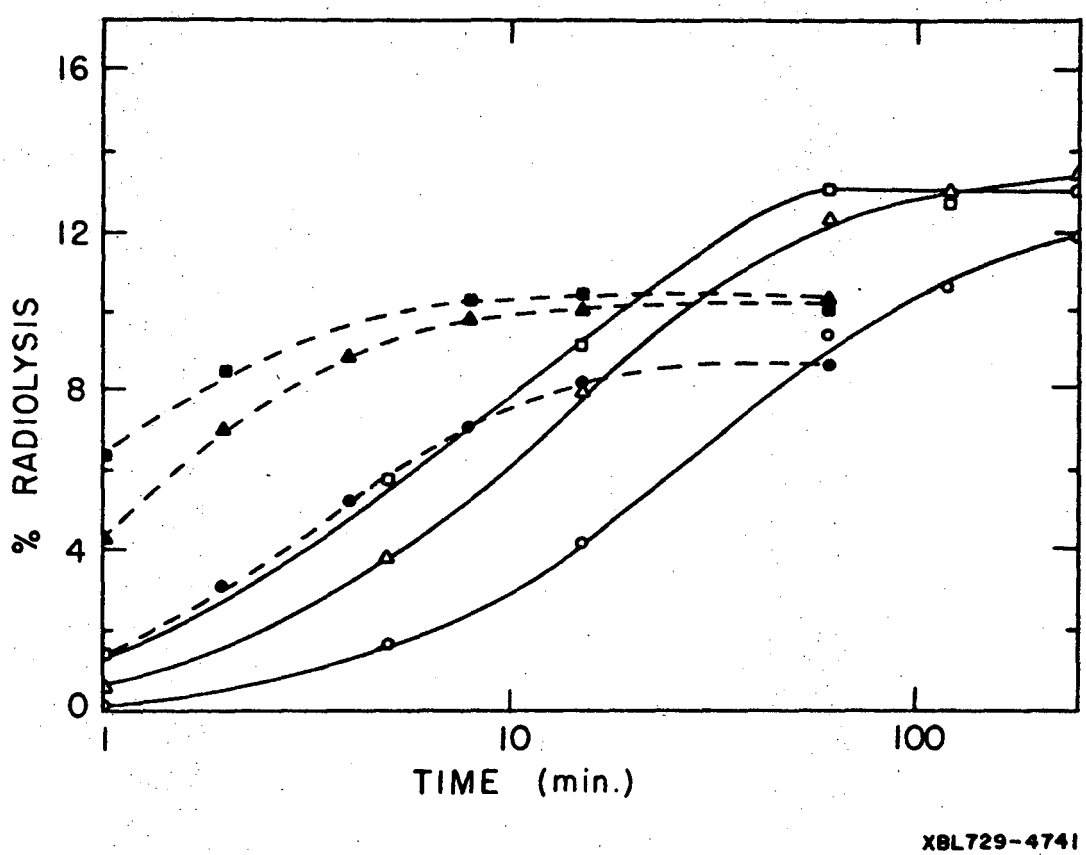

Figure 7. Radiolysis kinetics of choline chloride (50° and 71°) at different total doses. o, Δ, ◻: 1.25, 5.0, and 15.0 Mrad, respectively, at 50°. ●, ▲, ■: 1.25, 5.0, and 15.0 Mrad respectively, at 71°.

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