SOLID-STATE CHEMISTRY OF IRRADIATED CHOLINE CHLORIDE

Table of Contents

Results and Discussion

Results and Discussion

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SOLID-STATE CHEMISTRY OF IRRADIATED CHOLINE CHLORIDE

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ABSTRACT

The remarkable and unique sensitivity of crystalline choline chloride towards ionizing radiation has been further investigated. ESR studies at -196° indicate the presence of a biradical, $(CH_3)_3\overset{+}{N}\cdot\cdot\ CH_2CH_2OH$ ---- $Cl^{\cdot}$, that diffuses apart with rising temperature. These studies also indicate the presence of an ethanol monoradical. Thermoluminescence studies indicate that during γ-irradiation electrons get trapped on crystal imperfections. These electrons are released upon warming above room temperature. It has also been found that (1) the radiolysis can be induced at low temperature by transferring electrons from photodonors; (2) the radical decay is enhanced in the presence of photodonated electrons; (3) the radiolysis is retarded by the electron-accepting ambients; (4) the radiolysis is also retarded by doping the crystals with KI; (5) heating at 150° before irradiation leads to diminished radiolysis; (6) large, slowly grown crystals are more resistant to radiolysis than are microcrystallites; (7) the extent of decomposition is increased for a given radiation dose if the dose delivery is interrupted by periods of heating at 50°; (8) the radical decay is faster than the radiolysis; (9) the radiolysis can be enhanced by exposure to thermal electrons. These observations are interpreted as reflecting a prominent role for detrapped electrons in the radiolysis mechanism. It has also been found that choline chloride and choline bromide are the only analogs that give ethanol radical upon irradiation. This coupled with the fact that these are the only compounds which are abnormally radiation sensitive suggest that ethanol radicals are necessary for the chain mechanism. This is further confirmed by photoreduction of ethanol radicals at temperatures where the chain does not propagate, and the subsequent diminished radiolysis. Exposure to atomic hydrogen produces a large decomposition of choline chloride. These observations indicate that (a) radicals are formed and electrons are trapped upon irradiation and (b) during the subsequent thermal treatment, the detrapped electrons interact with ethanol radicals to form hydrogen atoms, which propagate the chain decomposition. A mechanism to explain these observations is proposed.

We have also made dc and microwave conductivity measurements. Our results suggest that electrons are the charge carriers in the α-form, while protons are probably the carriers in the β-form. It is proposed that the protonic conductivity may be responsible for the radiation-resistant nature of the β-form. The infrared studies support the phase transformation in choline chloride and further indicate that O-methylene protons play a key role in the radiolysis mechanism.

CHAPTER 1

GENERAL INTRODUCTION AND REVIEW

Compounds labeled with radioactive nuclei are extensively used in both physical and biological studies. In 1953 it was suggested by Tolbert et al.[1] that such compounds should be checked for radiopurity prior to use, as they may undergo self-radiolysis to an appreciable extent upon storage. A striking example is choline chloride, $[(CH_3)_3NCH_2CH_2OH]^+Cl^-$. This compound was synthesized with a ^{14}C label in a methyl group, with a specific activity of 13 μc/mg. After it had been stored for only nine months, at room temperature, it was found to be 63% decomposed by the β-rays from the ^{14}C. That the compound is extraordinarily sensitive to ionizing radiation was later confirmed by the irradiation of the unlabeled compound by ^{60}Co γ-rays. The main products were found to be trimethylamine and acetaldehyde. Quantitatively this self-irradiation sensitivity was given by $G_{(-M)} = 500$ (the $G_{(-M)}$ is defined as the number of molecules decomposed per 100 eV of energy absorbed). The normal range of $G_{(-M)}$ for non-vinyl compounds (which are susceptible to radiation-induced polymerization) ranges from 0.1 to 20.[2] In fact, with respect to simple molecular decomposition, choline chloride is the most radiation sensitive compound known. Under certain conditions of irradiation the $G_{(-M)}$ can be as high as 55,000.[3] Since choline chloride is thermally stable at temperatures up to about 200°, a minimum activation energy of the order of 1.0 eV for thermal decomposition is indicated. The observance of reaction with much smaller average energies in radiolysis can only be interpreted as evidence for a chain-decomposition mechanism.

The free radicals that are formed upon irradiation of choline chloride were investigated by Lindblom et al.[3] A tentative structure was assigned to the radical as $H_2C{\cdot}CH_2OH$. The electron spin resonance signal obtained by irradiation of selectively deuterated choline chlorides at the methyl, N-methylene, O-methylene, and hydroxyl positions supported this assignment. A chain decomposition mechanism was proposed, which required the observed radical to be in the form of a stabilized radical rather than the chain propagating species.

In an effort to find structural features that could be related to the anomalous radiation sensitivity of choline chloride, Lemmon et al. investigated the radiation sensitivity of nineteen different analogs of choline chloride.[4] Although a wide selection of different anions was tried and the methyl and ethanol groups were replaced with a wide variety of similar and differing groups, only the choline bromide showed an interesting sensitivity. Its $G_{(-M)}$ was about one-third that of choline chloride. Choline fluoride was not tried as it decomposes very quickly at room temperature (1-2 days), and is extremely deliquescent.

It was also reported in the same paper that the radiolysis can be deferred indefinitely at -196°. At room temperature the half life of radiolysis is about 4 hours. It was also found that the radiation sensitivity of choline chloride is observed only in the crystalline form. Lemmon et al. reported $G_{(-M)} = 3$ in solutions of varying concentrations (10 mg/ml to 400 mg/ml) in water and ethanol.[4]

Serlin reported that the radiolysis of crystalline choline chloride is dependent on temperature.[5] He obtained an increasing

$G_{(-M)}$ up to about 50° and a sudden drop in $G_{(-M)}$ somewhere between 50° and 150°. Later Shanley and Collin reported a phase transition at about 78°, wherein the choline chloride went from an orthorhombic to a disordered face centered cubic crystal form.[6] They found that the density of the high temperature polymorph (β-form) is about 10% lower than that of the <78°, radiation-sensitive crystals (referred to now as the α-form). They irradiated choline chloride at temperatures from 30° to 90°; $G_{(-M)}$ values increased up to about 73° and dropped markedly between 73° and 80°.

The crystal structure studies were extended by Senko and Templeton[7] and more recently by Hjortas and Sorum.[8] It was inferred from the bond length and angles that the nitrogen-methylene carbon bond (where the cleavage takes place during radiolysis) is unusually longer than normal, and that there is hydrogen bonding between the oxygen and chloride.

Lemmon and Smith used ^{14}C and deuterium labeling to study the radiolysis mechanism of choline chloride.[9] The ^{14}C radioactivity was found in the trimethylamine product when they started with methyl ^{14}C-labeled choline chloride, while it was entirely in the aldehydic carbon of acetaldehyde when O-methylene ^{14}C-labeled choline chloride was used. They inferred that the carbinol group of the ethanol moiety becomes the aldehyde group of the resultant aldehyde, and that the carbon atoms of the ethanol moiety and of methyl groups maintain their identities during the mechanism leading to the production of acetaldehyde and trimethyl amine. The acetaldehyde obtained as the decomposition product from selectively deuterated choline chlorides was studied by the use of a mass spectrometer. From the intensity and positions of mass peaks obtained, they inferred that, during the radiolysis, (a) no hydrogens are transferred to or from the trimethyl amino group, (b) the hydrogens of the ethanol moiety are highly mobile for intramolecular exchanges, and (c) some intermolecular hydrogen transfer takes place.

In a search for the radical termination mechanism, Smith and Lemmon reported that the possibility of radical termination by the dimerization to a butanediol or disproportionation to ethanol is very small.[10] Under conditions of irradiation where one would expect substantial chain terminations to occur, they found negligible amounts of butanediols and ethanol. Based on their results they suggested that the chain propagating radical terminates by reaction with another radical (possibly $(CH_3)_3\overset{+}{N}\cdot$) that propagates into its vicinity.

Ackerman and Lemmon continued work to make a detailed product inventory of the products formed upon radiolysis of crystalline choline chloride.[11] At least 95% of the products were accounted for by trimethylamine and acetaldehyde. Among the minor products were H_2, approximately 2.7%; CH_4, approx. 2.3%; CH_3Cl, approx. 0.2%; polymers and Cl_2, <1%. It was inferred that trimethylamine and acetaldehyde are the result of chain decomposition, while the minor products come from ordinary, random, radiolytic processes.

The extreme radiation sensitivity of crystalline choline chloride, which is dependent on its crystal form, and the very simple radiolysis products make it a unique system for the study of energy-transfer mechanisms in crystals. Choline and its derivatives are very important biological components (for example, in the transmission of nerve impulses). If one were to assume precise, though as yet unknown, alignments of choline molecules in nerve synapses, one can speculate that our studies of energy transmission in choline crystals may someday be understood to be of importance to biology.

CHAPTER II

ELECTRON SPIN RESONANCE STUDIES OF γ-IRRADIATED CRYSTALLINE CHOLINE CHLORIDE AND SOME OF ITS ANALOGS

It was reported by Lemmon et al. that free radicals are formed upon the e^-- or γ-irradiation of choline chloride.[2] Lindblom, Lemmon and Calvin extended the studies to assign a structure to the radicals formed.[3] The ESR spectrum obtained was not well resolved at -196° and, therefore, all their results were obtained at room temperature. It was also suggested that these radicals participate in the chain mechanism resulting in the radiolysis of choline chloride. However, other analogs, with the exception of choline bromide, are radiation resistant. In order to investigate the role of radicals formed upon γ-irradiation in the radiolysis mechanism, we have extended these studies of choline chloride to a temperature range from -196° to 100° and also to some of its analogs in the same temperature range.

Experimental

Choline chloride was purchased from J. T. Baker and Company. It was dissolved in 96% ethanol and converted to choline hydroxide, $[(CH_3)_3NCH_2CH_2OH]^+OH^-$, in a darkened flask (to avoid light exposure) by the addition of a slight excess of Ag_2O. After being thoroughly agitated, the solution was filtered through a very fine sintered glass funnel protected by a layer of celite. It is difficult to remove the last traces of the AgCl that is formed; it is also difficult to remove all of the Ag_2O. Therefore, to remove these last traces the filtrate is shaken with activated charcoal and refiltered through another very fine sintered glass funnel. The filtrate is now converted to choline bromide, $[(CH_3)_3NCH_2CH_2OH]^+Br^-$, choline iodide $[(CH_3)_3NCH_2CH_2OH]^+I^-$, and choline sulfate, $[(CH_3)_3NCH_2CH_2OH]_2^+SO_4^=$, by the addition of the equivalent amounts of HBr, HI, and H_2SO_4. The solution is then evaporated to dryness in a rotary evaporator at room temperature, giving polycrystalline choline bromide, choline iodide, and choline sulfate. The propyl analog, $[(CH_3)_3NCH_2CH_2CH_2OH]^+Cl^-$, chloro analog, $[(CH_3)_3NCH_2CH_2Cl]^+Cl^-$, and the ethyl analog, $[(C_2H_5)_3NCH_2CH_2OH]^+Cl^-$, were prepared earlier in this laboratory.[4] The choline choride and these analogs were purified by triple crystallization out of ethanol solution by slow evaporation. The purified compounds were redissolved in absolute ethanol in a dry box and precipitated by the addition of tenfold excess of precooled (-78°) anhydrous diethyl ether. The precipitated material was washed with cold ether and dried on a vacuum line. The dried pure compounds were stored in a dry box. The material thus obtained was of very small particle size and will be called polycrystalline hereafter. The compound's purity was ascertained by the quantitative elemental analysis; the C, H, and N analyses were always within 0.2% of the calculated values. The storage and handling of these compounds in a dry box is necessitated by the fact that they are all extremely hygroscopic.

Approximately 50 mg of each of the samples were filled in ESR signal-free quartz tubes, obtained from Varian Associates, and fused to standard 14/35 quartz vacuum joints. The tubes were then attached to a vacuum line via a "cow" (capable of attaching six tubes at a time), and the samples were dried for 1 hour at 100° under a pressure of 10^{-4} torr. The small amounts of sample sticking to the side of the tube was removed by heating the tubes with a hot flame (vaporizing and removing such material) and the tubes were then sealed under vacuum.

The sealed tubes were then irradiated at -196° in a dewar by a 3000 curie ^{60}Co γ-ray source for 1 hour. The ^{60}Co γ-ray source consisted of a rotaing stage surrounded by sixteen concentric ^{60}Co rods. To assure maximum uniformity the sample tubes were arranged concentrically in the dewar by a tube holder. The dose was calculated from the exposure time and the dose rate. The latter had previously been determined by $FeSO_4$ dosimetry.[12] The dose rate from the ^{60}Co source could be varied by changing the radial position of the ^{60}Co rods. The maximum dose rate used was 5 Mrads/hour. ^{60}Co has a half life of approximately 5.3 years and thus a correction to take account of the decay of ^{60}Co radioactivity was applied in calculating the dose. The samples used here received a total dose of 5 Mrads. Although signal-free quartz tubes were used for ESR studies, they developed F-centers and other radiation damage due to the highly penetrating γ-rays and the large doses. The signals from these centers were eliminated in the following way. The upper cleaned end of the irradiated tube was heated to about 400° while cooling the lower end, containing the sample, with liquid nitrogen at -196°, thus annealing the signal from the upper end. Then the tubes were inverted (still in liquid nitrogen), transferring all the sample to the annealed end. In this way the ESR signal recorded was due only to the sample.

The ESR spectra at various temperatures were recorded on a Varian Model E-3 spectrometer. The sample temperatures were varied using a variable temperature assembly associated with the spectrometer.

Results and Discussion

A. Choline Chloride

It has been generally assumed that the radical created in the sample during the γ-irradiation at -196° and the one observed at room temperature are identical, the only difference being the loss, at the low temperature, of the motional narrowing of the ESR spectrum. If this is true, then the ESR spectrum of a sample irradiated at -196° should be similar to the one which is irradiated at -196°, warmed to some higher temperature, and then cooled to -196° (the motional narrowing is reversible). Figure 1 shows the ESR spectrum of a polycrystalline sample of choline chloride γ-irradiated at -196° and recorded at the same temperature (no warm up). Figure 2 shows the corresponding spectrum of an identical sample irradiated at -196°, warmed to -20°, and then recooled to -196°. It is obvious that some irreversible changes occur during the warming; for instance, the shoulders indicated by the arrows in Figure 1 have completely disappeared. These changes have been recently observed by Symons,[13] who interpreted them as reflecting the disappearance of $\cdot ClOH^-$ 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. In addition, the formation of $\cdot ClOH^-$ radicals would depend upon the presence of water, but we have found unchanged ESR spectra regardless of whether our deliquescent crystals were exposed to atmosphere or to conditions of rigorous moisture exclusion (24 hours evacuation at $< 10^{-7}$ torr pressure at 100°). Futhermore,

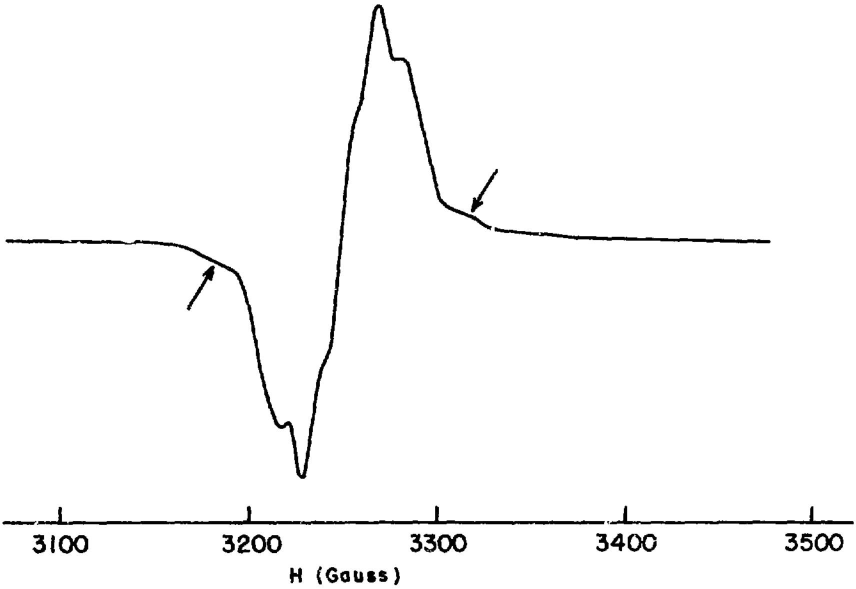

Figure 1. The ESR spectrum of γ-irradiated polycrystalline choline chloride: irradiation at -196°, spectrum at -196°.

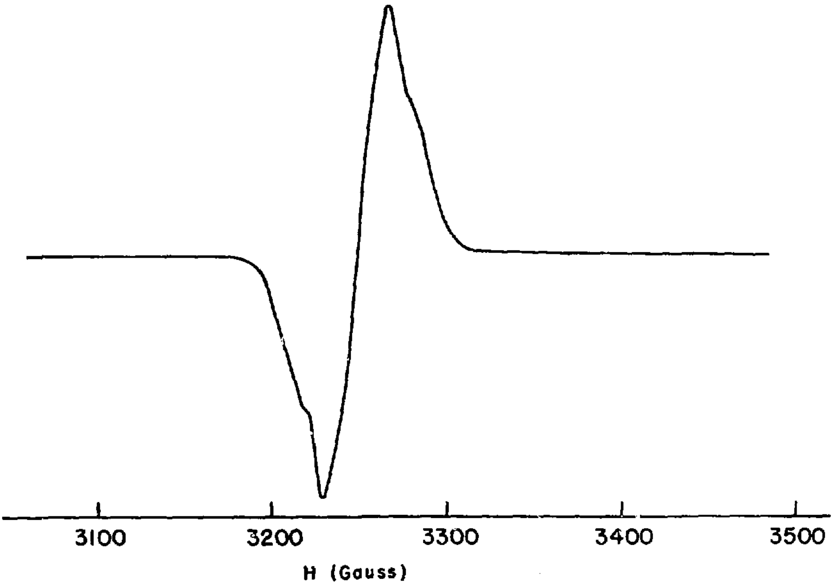

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Figure 2. The ESR spectrum of γ-irradiated choline chloride: irradiated at -196°, warmed to -20°, and spectrum recorded at -196° after recooling.

Symons found that his signal dur to $\cdot ClOH^-$ radicals disappeared upon warming to -163°. The shoulders in our spectrum did not decay completely up to about -40° (see below). The $\cdot Cl_2^-$ radical signal reported by Symons, and found by us also, does indeed decay at about -110°. However, it is possible that a small part of the shoulders may also be due to $\cdot ClOH^-$ radicals.

In Figure 3 we have recorded the ESR spectrum (at -166°) of a γ-irradiated polycrystalline sample in 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 ($\Delta M_s = 2$).[14] The two most plausible explanations for this 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] $(CH_3)_3N^+ \cdot\cdot CH_2CH_2OH - \cdot Cl^-$, or (2) an interradical interaction between two ethanol radicals. We believe that the second explanation is not probable, because Smith and Lemmon[10] had searched for, but found only insignificant amounts of, either 1, 4- or 2, 3-butanediol as products of the choline chloride radiolysis. If the biradical was $HO\text{-}CH_2\text{-}H_2C\cdot\cdot CH_2\text{-}CH_2OH$, then its "dimerization" reaction would be expected to give either or both of the butanediols. It therefore appears that our $\Delta M_s = 2$ absorption is by an intraradical coupling, namely, by a biradical with the formula given above. No trimethylamine radicals were seen, presumably because of excessive broadening by the nine protons or rapid spin-lattice relaxation. However, Symons has reported that these radicals are observed in his ESR spectrum of

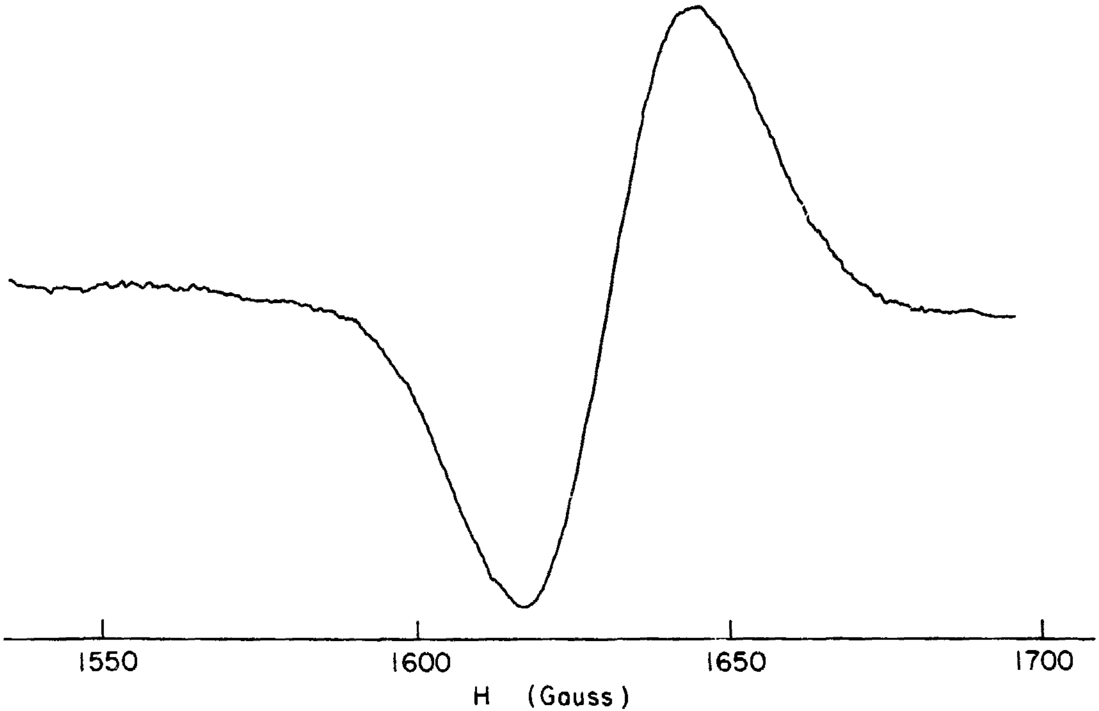

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Figure 3. The biradical ESR spectrum in γ-irradiated choline chloride at -166° corresponding to the $\Delta M_S = 2$ transition.

γ-irradiated choline chloride.[13] The existence of such "pairwise trapping" has been frequently reported.[15-20]

In general, the zero-field splitting parameters (D and E)[21] for paramagnetic species are given by

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

where hν 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/G), and H is the magnetic field at which the biradical is observed. For radical pairs, E is usually assumed to be approximately zero.[22] For our case D was found to be 140 G. D is related to R, the interradical distance by the equation (for random orientation)

$$D = 3\beta g/2R^3$$

For our spectrum at -196°, this distance was found to be approximately 6 Å.

The biradical also has an absorption in the $\Delta M_s = 1$ (monoradical) region. The ratio of the biradical transition probabilities at $\Delta M_s = 2$ and $\Delta M_s = 1$, respectively, is given by (also for random orientation)[22]

$$\frac{I_2}{I_1} = \frac{4}{15} (\frac{D}{H_0})^2$$

where H_0 is the field value for the $\Delta M_s = 1$ transition. This ratio is found to be 5×10^{-4} in our case (D being 140 G). By performing double integration of the measured $\Delta M_s = 1$ and $\Delta M_s = 2$ ESR derivative 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 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 $\Delta M_s = 2$ transition/intensity of the $\Delta M_s = 1$ transition) is

$$Q = \frac{I_2}{I_M + I_1} = \frac{I_1 \frac{4}{15} (\frac{D}{H_0})^2}{I_M + I_1} ; \qquad \frac{I_M}{I_1} = \frac{4}{15Q} (\frac{D}{H_0})^2 - 1$$

For our case $Q = 10^{-4}$, which gives $\frac{I_M}{I_1} = 4$, meaning that 20% of the measured intensity at the $\Delta M_s = 1$ transition can be attributed to the biradical. Thus, the marked peaks in Figure 1 may belong to the biradical, since the separation between them fits the calculated zero-field splitting parameter of 140 G.[22]

Temperature effects were also observed in the $\Delta M_s = 1$ and $\Delta M_s = 2$ transitions. An irradiated (160°) sample was warmed at a given temperature for approximately 10 min., recooled to -166° (the lowest temperature attainable in the variable temperature assembly), and the spectrum recorded. The same sample was then warmed to another annealing temperature (10 min.) and again recooled to -166° for another redording of the ESR spectrum. This way we eliminated influences of such reversible temperature effects as motional narrowing and magnetic susceptibility.

In Figure 4, curves (a) and (b) give the intensity in arbitrary units (peak to peak height) of the $\Delta M_s = 1$ and $\Delta M_s = 2$ transitions, respectively, as a function of the annealing temperature. The signals

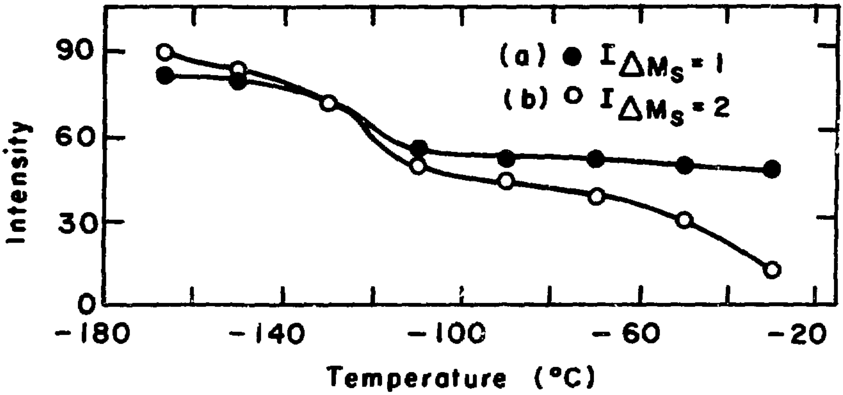

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Figure 4. (a) ESR intensity of the monoradical at -166° in γ-irradiated choline chloride (irradiated at -196°) as a function of annealing temperature; (b) ESR intensity of the biradical at -166° in choline chloride (irradiated at -196°) as a function of annealing temperature.

decay simultaneously up to about -110°. However, at higher temperatures the biradical signal continues to show considerable decay while the monoradical signal stays almost constant. The fact that the $\Delta M_s = 1$ transition signal stays practically constant for annealing temperatures higher than -110° indicates that the change in the region -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 from -130° to -110° to a change in the nature of the monoradical. Comparison of Figures 1 and 2 clearly shows the change in the radical spectrum upon warming .the spectrum of Figure 2 is no different if the sample is warmed only to -110° before the re-cooling to -196°); however, there are gradual changes from -196° to -130°.

We visualize the radical formation as follows: The ionizing radiation creates at -196° a "precursor" monoradical. It is essentially 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 (about 0°) 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 is also presumed to be related to the monoradical's transformation.

The explanation for the continued decreas in the biradical's signal above -110° can be that the two monoradicals (the ethanol and the trimethylamine radicals) are diffusing away one from the other and, therefore, the interaction between the coupled spins decreases. In order to test the validity of this explanation, the values of the zero-field splitting parameter D were calculated for different annealing temperatures (after cooling back to -166°). Within the limit of our accuracy, D was found to decrease with an increase in the annealing temperature. This implies that the interradical distance R increases.

We have also plotted in Figure 5 (a) the ratio R (= peak to peak height of the $\Delta M_s = 2$ transition/peak to peak height of the $\Delta M_s = 1$ transition) at various annealing temperatures (no cooling back to -166°). Figure 5 (b) gives the same ratio after the sample has been recooled from the annealing temperature back to -166° (claculated from Figure 4). The difference between the Q values clearly indicates that the biradical interaction is temperature dependent.

We need to comment on our failure to observe trimethylamine radical. This failure may be due to a low transition probability of this radical. In addition, this monoradical may disappear by interaction with the trapped electrons that are depopulated below -10° (see next chapter).

The ESR observations are in accord with the mechanism that was proposed earlier[3] to account for the radical formation in irradiate 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. The biradical disappears upon warming before the chanin propagation

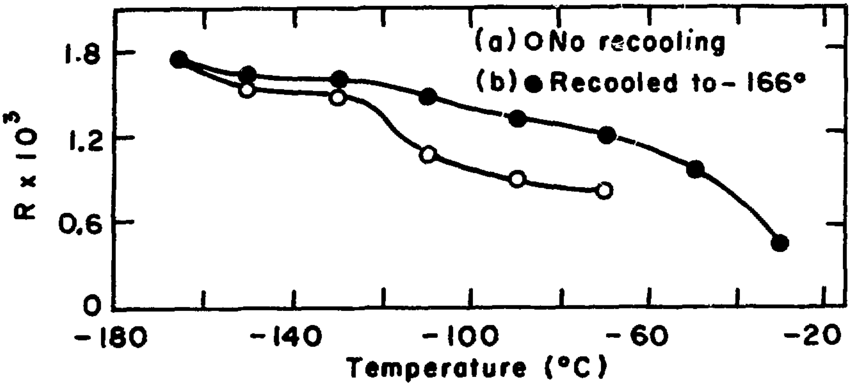

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Figure 5. (a) The ratio R of peak to peak height of the biradical and the monoradical in choline chloride (irradiated at -196°) at various temperatures; (b) the same ratio at -166° after the sample is recooled from various annealing temperatures.

begins, while the monoradical participates in the chain radiolysis. Much of the foregoing observations concerning the biradical in irradiated choline chloride have been published.[23]

In order to shed more light on the radical which participates in the radiolysis process, room temperature studies were made of γ-irradiated single crystals of choline chloride. The spectrum obtained at room temperature (c-axis perpendicular to the static magnetic field) is a quintet with intensity ratios of 1:2:2:2:1, Figure 6 (a). At certain orientations the main lines of the quintet exhibit an additional doublet splitting with a 1:1 intensity ratio, Figure 6 (b). The splitting of the quintet lines is found to be 12 G while the doublet splitting of the main lines is 4 G. Similar observations were also reported by Fingerman and Lemmon. This type of spectrum corresponds to four protons with interaction constants 1:3:3:6. It is hard to visualize such interaction constants of the four protons, but there are other evidences for such an assignment. Lindblom suggested, on the basis of NMR spectra of selectively deuterated choline chlorides, that the N-methylene has less of a barrier to rotation than the O-methylene.[25] In addition, the ESR spectrum of N-methylene deuterated choline chloride obtained by Lindblom _et_ _al._[3] may be considered as a four-line spectrum rather than a three-line. Two unequivalent protons would indeed give a four-line spectra. Therefore, our single crystal work and Lindblom's reported results fit quite well with the assignment in which N-methylene protons are equivalent and the O-methylene protons inequivalent. One of the O-methylene protons has interaction twice as strong as the N-methylene proton, while the other only one-third as strong. This could

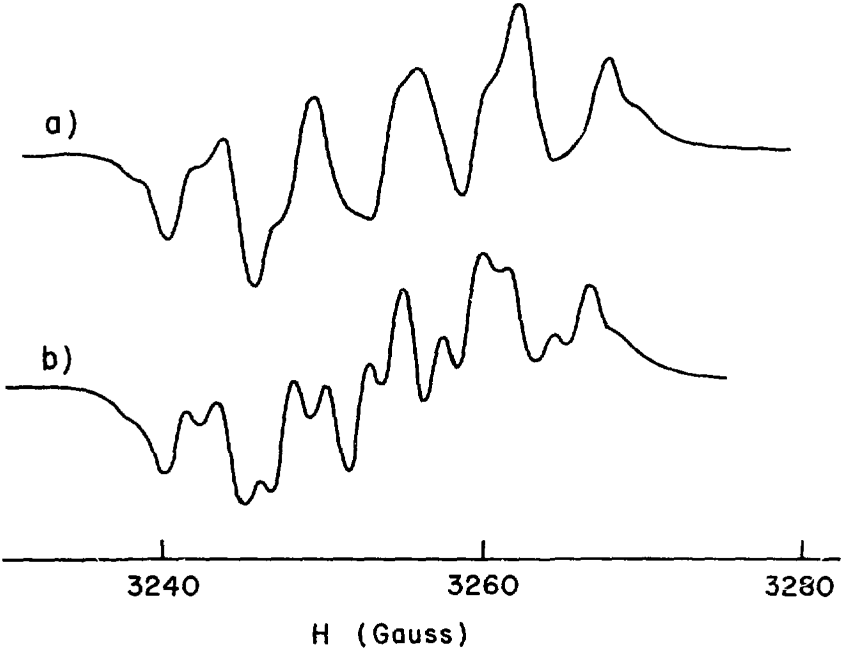

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Figure 6. Curves a and b correspond to the ESR spectra of a γ-irradiated choline chloride single crystal at two different orientations of the a-b axis with respect to the static magnetic field (c axis is perpendicular to the static magnetic field). Spectra recorded at 23°.

happen if the unpaired electron is closer to one of the protons belonging to O-methylene group. The rotating N-methylene group protons would have equal interactions.

Although the ethanol radical is essentially stable up to 0°, it starts decaying with increasing temperatures. At room temperature the half life is approximately 4 hours, at 50° approximately 4.5 min., at 70° approximately 1 min., and the signal disappears instantaneously at about 80°, where the phase transition takes place. The spectrum of the radical at 5° is well resolved and is shown in Figure 7. The nature of the spectrum remains unchanged for wide variations in irradiation doses and also if the radical decays by a hundredfold. Power-saturation experiments also showed that all the lines were saturated to the same extent. These observations indicate that the ESR spectrum corresponds to a single radical, which we have referred to as the ethanol radical.

B. Choline Analogs

The ESR studies of choline analogs were carried out similarly to the studies of choline chloride. The samples were γ-irradiated at -196° and the spectra also recorded at -196°. They were then annealed at some higher temperature for 5 min., cooled back to -160° and the spectra recorded. Since the spectra were better resolved at 5°, the samples were recooled only to 5°, from the higher (than 5°) annealing temperatures, to record the spectra. In these studies the main goal was to compare the radicals formed in these analogs, and the temperature effects on them, with the radicals formed in choline chloride. The results of these studies, in the main, are the following. The few

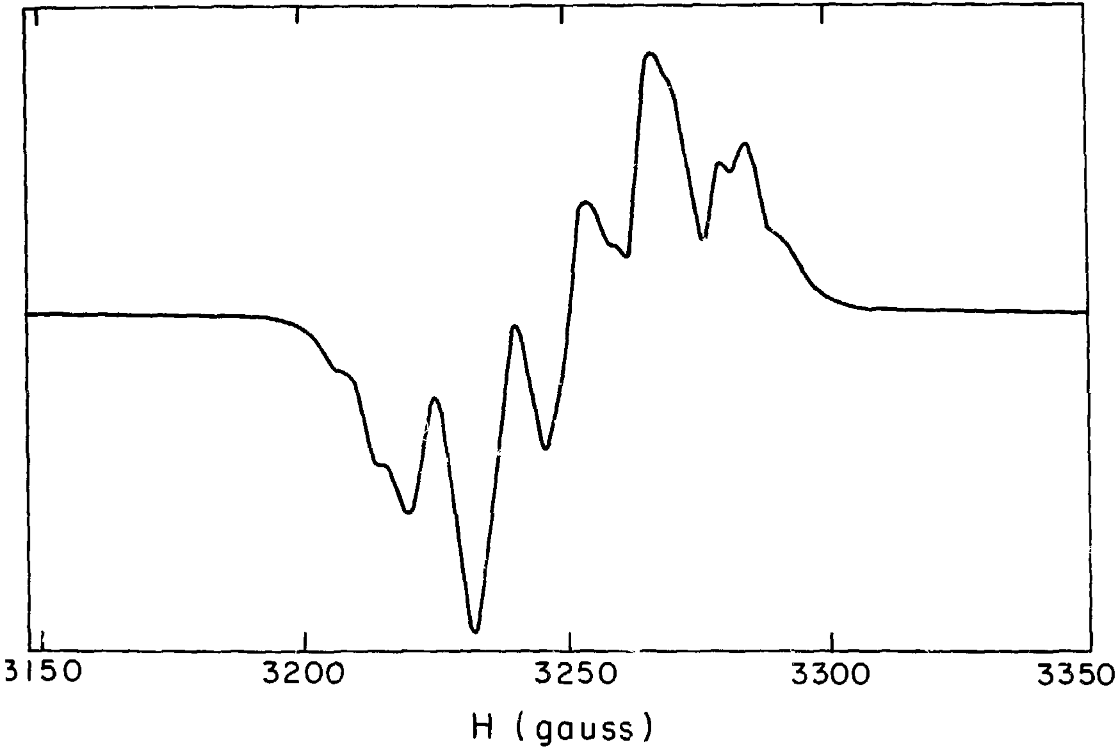

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Figure 7. The ESR spectrum of polycrystalline choline chloride: irradiated at -196°, warmed to 5°, and spectrum recorded at 5°.

spectra presented are only those that show changes in spectral characteristics.

(1) Choline bromide, $[(CH_3)_3NCH_2CH_2OH]^+Br^-$. The ESR spectrum of γ-irradiated choline bromide at -196° is shown in Figure 8a. The hyperfine splitting (marked by arrow) at low magnetic field may be due to $Br_2^-\cdot$ or Br· radicals. The hyperfine splitting decays upon sample warming and disappears completely at -60° in 5 min. There is also a small signal due to biradicals (beyond the magnetic field range of the spectrum shown). The spectral characteristics change slowly by annealing the sample for 5 min. at temperatures up to 5° (Figure 8b and 8c). Although not shown in Figure 8, the general decay is small in the temperature range -160° to -90°. The decay between -90° and 25° is faster than that of the radical in choline chloride and above 25° is slower than in the chloride. The signal disappears instantaneously at 100° (probably due to a phase transition). The nature of the radical also changes by annealing at about 80° (Figure 8d). The spectrum recorded at 5° (Figure 8e) is similar to that obtained with choline chloride (cf. Figure 7).

(2) Choline iodide, $[(CH_3)_3NCH_2CH_2OH]^+I^-$. The ESR spectrum of γ-irradiated choline iodide at -196° is shown in Figure 9a. There is also small microwave power absorption at magnetic fields of approximately 2600, 2650, 2800, and 2950 G, possibly due to I·, disappearing at -110°. There is no detectable biradical signal. The nature of the radical seems to change by annealing the sample up to -90°, above which the signal remains unchanged (Figures 9b and 9c). However, it decays slowly up to -10° and above room temperature decays very

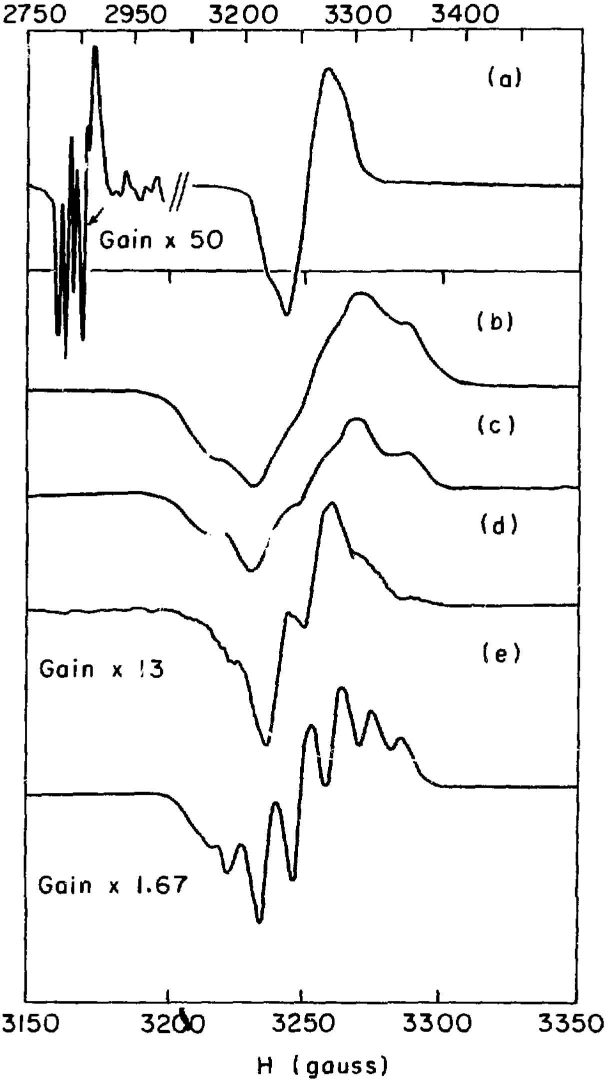

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Figure 8. The ESR spectra of γ-irradiated polycrystalline choline bromide: (a) irradiated at -196°, spectrum at -196°; (b) spectrum at -160°; (c) annealed at 5°, spectrum at -196°; (d) annealed at 80°, spectrum at 5°; (e) annealed at 5°, spectrum at 5°.

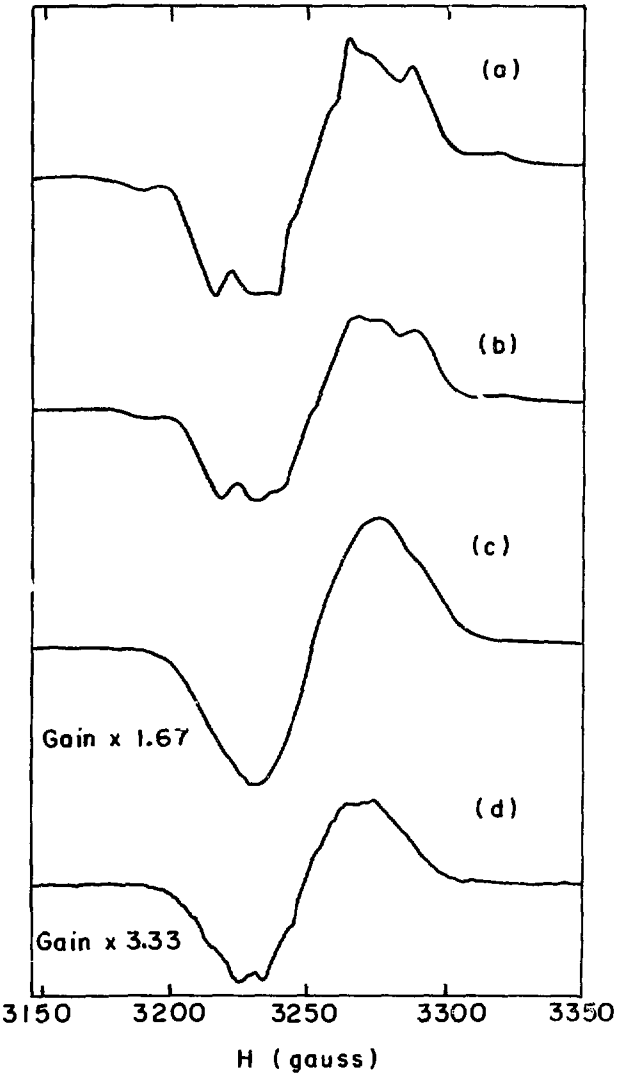

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Figure 9. The ESR spectra of γ-irradiated polycrystalline choline iodide: (a) irradiated at -196°, spectrum at -196°; (b) spectrum at -160°; (c) annealed at -90°, spectrum at -160°; (d) annealed at 5°, spectrum at 5°.

fast, disappearing at 50° within 5 min. The spectrum recorded at 5° (Figure 9d) has no similarities to the ethanol radical in choline chloride.

(3) Choline sulfate, $[(CH_3)_3NCH_2CH_2OH]_2^+SO_4^=$. The ESR spectrum of γ-irradiated choline sulfate is shown in Figure 10a. The small side bands disappear upon annealing at -110°. The biradical signal at -196° also disappears at -160°. The central part of the spectrum does not change significantly upon annealing at temperatures up to 25°, and the decay is also small. However, annealing above 25° brings in substantial decay and change in the nature of the radical. The transformed radical is stable even at 100° (Figures 10b, 10c and 10d).

(4) Chloro analog, $[(CH_3)_3NCH_2CH_2Cl]^+Cl^-$. The spectrum of the chloro analog recorded at -196° is shown in Figure 11a. The low intensity side bands continue to decay, but disappear only at an annealing temperature of -30°. There is no biradical signal. The spectral characteristics change quite significantly by annealing up to -90° (Figures 11b and 11c). However, the signal continues to decay above -90° and disappears completely by annealing for 5 min. at 40°. The spectrum recorded at 5° has no similarities to the radical in choline chloride (Figure 11d).

(5) Propyl analog, $[(CH_3)_3NCH_2CH_2CH_2OH]^+Cl^-$. The ESR spectrum of γ-irradiated propyl analog at -196° is shown in Figure 12a. There is very small biradical signal decaying at -160° completely. The spectral characteristics change very significantly upon annealing at -160° and -130° (Figure 12b). Above -130° the signal decays slowly up to the annealing temperature of -30°. Above this temperature it starts decaying faster, but slower compared to the ethanol

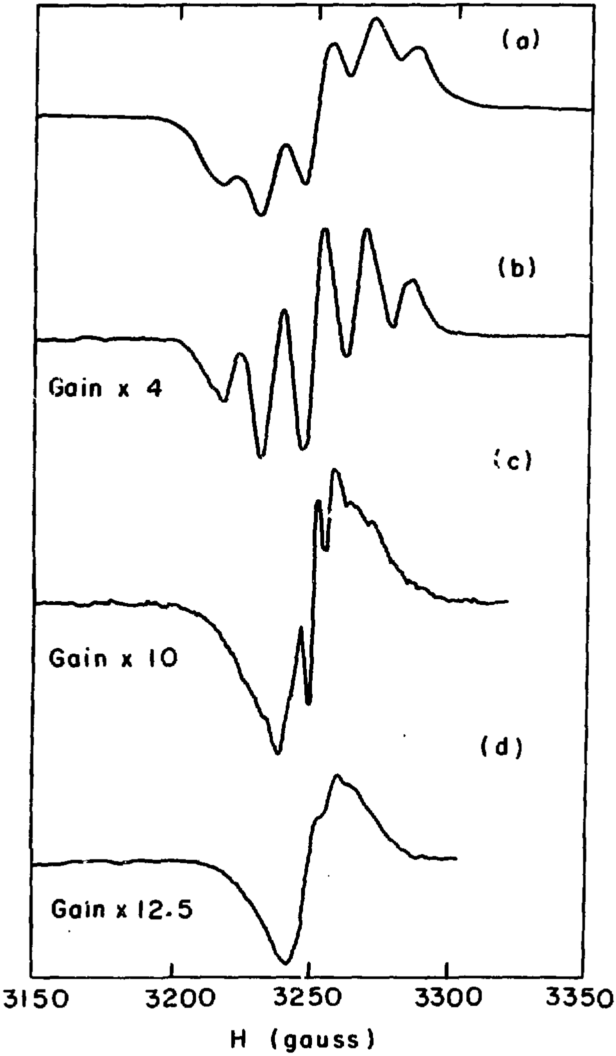

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Figure 10. The ESR spectra of γ-irradiated polycrystalline choline sulfate: (a) irradiated at -196°, spectrum at -196°; (b) annealed at 5°, spectrum at 5°; (c) annealed at 50°, spectrum at 5°; (d) annealed at 100°, spectrum at 5°.

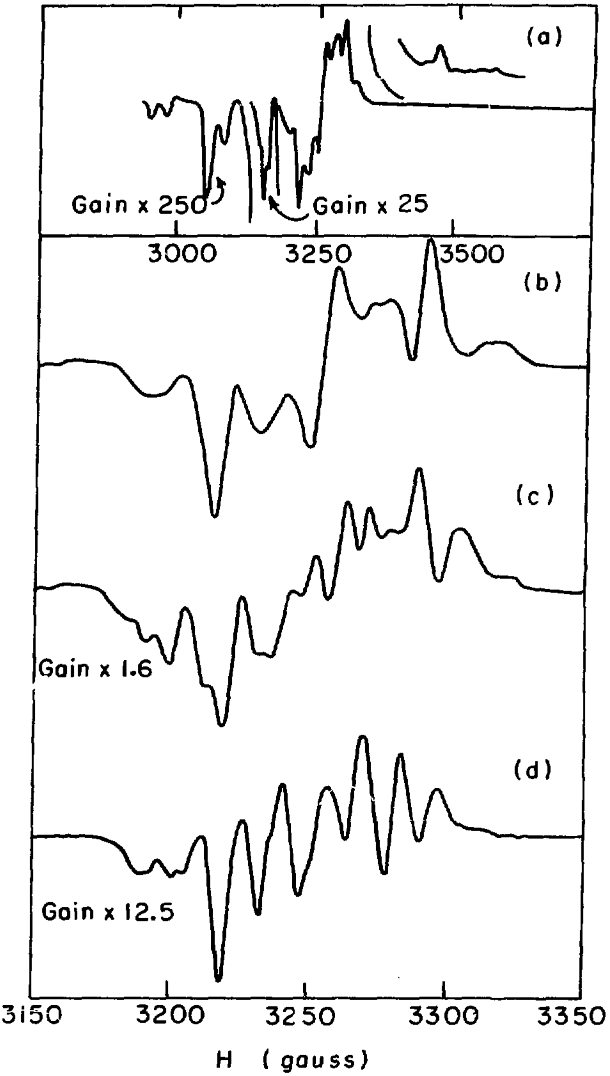

Figure 11. The ESR spectra of γ-irradiated polycrystalline chloro analog of choline chloride, $[(CH_3)_3NCH_2CH_2Cl]^+Cl^-$: (a) irradiated at -196°, spectrum at -196°; (b) spectrum at -160°; (c) annealed at -90°, spectrum at -160°; (d) annealed at 5°, spectrum at 5°.

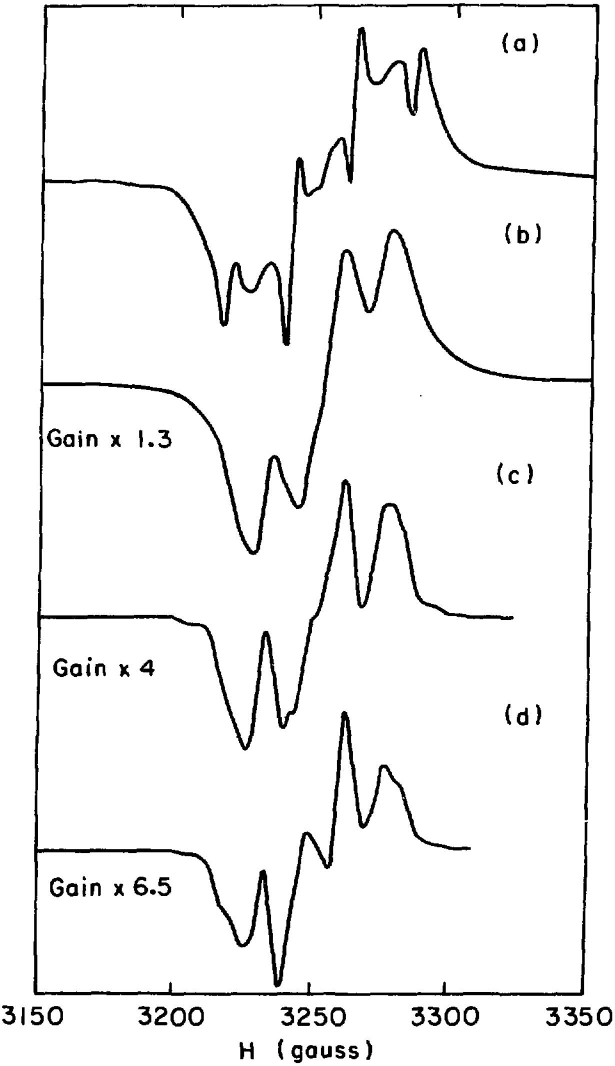

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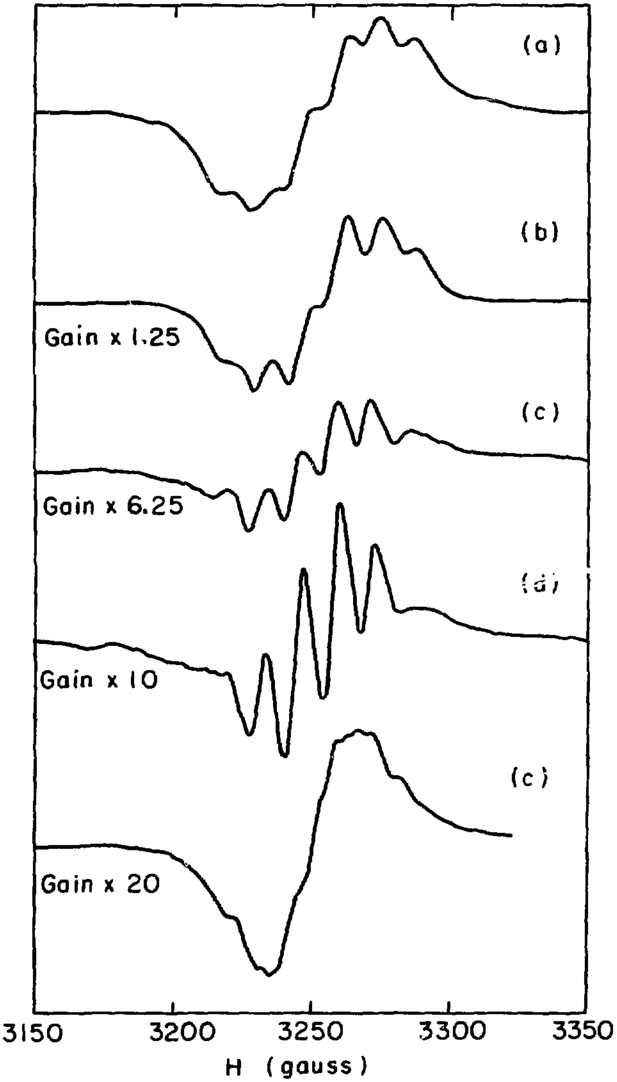
Figure 12. The ESR spectra of γ-irradiated polycrystalline propyl analog, $[(CH_3)_3NCH_2CH_2CH_2OH]^+Cl^-$: (a) irradiation at -196°, spectrum at -196°; (b) annealed at -130°, spectrum at -160°; (c) annealed at 50°, spectrum at 5°; (d) annealed at 80°, spectrum at 5°.

radical. The spectrum at 5° is similar to the one at -160°. However, annealing above room temperature changes the characteristic spectrum again (Figure 12c). The signal continues to decay but is still present at 100° after heating for 5 min. The spectrum after annealing at 80° for 5 min. is shown in Figure 12d.

(6) Ethyl analog, $[(C_2H_5)_3NCH_2CH_2OH]^+Cl^-$. The ESR spectrum of ethyl analog at -196° is as shown in Figure 13a. There are two very weak side bands at magnetic field values of 3040 and 3080 G. These disappear upon annealing at -160°, but a new broad peak is found at H = 2975 G. This peak is stable up to -90°, decaying above that, and disappears at -30°. There is biradical signal decaying at -160°. The main radical shows some decay and change in spectral features by annealing up to -30° (Figure 13b). Above -30° the radical decays very fast up to 5°. The spectrum recorded at 5° is shown in Figure 13c. Above 5° the signal seems to build-up to 50°, and shows some changes (Figure 13d), above which it decays and transforms into a different radical which decays only slowly even at 100° (Figure 13e).



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<u>Figure 13.</u> The ESR spectra of γ-irradiated polycrystalline ethyl analog, $[(C_2H_5)_3NCH_2CH_2OH]^+Cl^-$: (a) irradiation at -196°, spectrum at -196°; (b) annealed at -30°, spectrum at -160°; (c) annealed at 5°, spectrum at 5°; (d) annealed at 50°, spectrum at 5°; (e) annealed at 100°, spectrum at 5°.

Conclusion

From the results of the electron spin resonance studies, it appears that the radical formed upon γ-irradiation of choline bromide is also the same ethanol radical as in choline chloride (at least above 5°). The small differences may be due to different matrices in the two analogs (Br^- anion in place of Cl^-). However, the radicals formed in the rest of the analogs are not ethanol radicals. This is very interesting, because choline chloride and choline bromide are the only choline analogs which are radiation sensitive. Therefore, it can be safely proposed that ethanol radicals are essential for the radiolysis of γ-irradiated cholines and that they are the ones which participate in the chain mechanism.

CHAPTER III

THE ROLE OF FREE ELECTRONS IN THE RADIOLYSIS OF CHOLINE CHLORIDE

It has been reported earlier that the radiolysis of choline chloride will not take place if the irradiation (and subsequent storage) is done at -196°.[4] The radiolysis develops gradually over several hours at room temperature and much faster at higher temperatures (but below 78°). At 78°, choline chloride undergoes crystal phase transformation from an α form (orthorhombic) to a β-form (face-centered cubic) and the radiolysis rate is drastically reduced. Since the radiolysis of the α-form does not proceed at -196°, it appears that thermal stimulation is required either for the diffusion of radicals (or other reactive species) or for the release of trapped electrons. Thr trapping of electrons in solid organic compounds upon irradiation is a common phenomenon.[26] It is probable that electrons are trapped during irradiation, either on pre-existing crystal defects or ones created during irradiation. We have found evidence for such electrons in γ-irradiated choline chloride. Such electrons would be released upon warming of the sample. In order to investigate a possible involvement of detrapped electrons in triggering a chain decomposition, we have observed the effects (on the α-form's radiolysis) of prior thermal treatment, of added electron accepting ambients, of photoelectron transfers, of different crystal sizes, and of free thermal electrons.

Experimental

Thermoluminescence. The instrument used for the study of thermoluminescence was a Harshaw Thermoluminescence Analyzer (Model 2000). In its original form, the heating rate was very fast (about 150°/min.) and non-linear; in addition, the temperature readings were incorrect. Therefore, an external temperature programmer was assembled in this laboratory, in which the rate of heating was linear and also variable from slow to high rates (7.5° to 120°/min.). It also made possible steady-state temperature studies. The sample could be heated quickly to any predetermined temperature, and then left at that temperature for kinetic studies. Temperature calibrations were made with compounds of known melting points. All thermoluminescence experiments were done with a temperature rise rate of 20°/min. The instrument's photomultiplier tube has a S-11 response (300-640 nm).

Choline chloride purification. For the experiments involving determination of the extent of radiolysis we used the methyl-^{14}C-labeled choline chloride. It was obtained, in ethanol solution with a specific activity of 3.8 mCi/mmol, from the New England Nuclear Co. The labeled compound was diluted with ordinary choline chloride to bring it to a convenient specific activity of 140 μCi/mmol. The solution was converted to the base form by adding a slight excess of Ag_2O (to avoid photolysis of the silver salt and choline base, the flask was covered with a black cloth); the filtrate was then evaporated to dryness in a rotary evaporator. This procedure helped to remove most of the trimethylamine hydrochloride present as radioimpurity in the original choline chloride. The residue was redissolved in 96% ethanol; to this solution was added slightly more than 1 equivalent of 12 N hydrochloric acid. This was used as a stock solution and, for each experiment, an aliquot was withdrawn, evaporated to dryness, and the residue was dissolved in the minimum amount of absolute alcohol.

The latter was mixed with a large excess (1:10) of cold (-78°) diethyl ether to give a precipitate of finely divided polycrystalline choline chloride. To prepare large crystals of choline chloride (2-3 mm along the c-axis), the solution was allowed to evaporate slowly. To minimize self-radiolysis, the precipitation or crystallization was carried out only a few hours before use. In all samples there was a residual 0.1-0.3% of radioimpurity —— mostly trimethylamine hydrochloride (TMA). This resulted principally from self-radiolysis of the material during handling at room temperature. For experiments where radiolysis was not to be determined we used ordinary choline chloride.

Unless otherwise specified, irradiations were carried out in sealed, evacuated tubes, for 1 hour, at -196°, in the ^{60}Co γ-ray source at a dose rate of approximately 3 Mrads/hour.

The analyses for amounts of decomposition were accomplished by unidirectional paper chromatography followed by autoradiography and liquid scintillation counting. An approximately 5 λ aliquot out of the 1 ml solution of choline chloride in methanol, containing 1 mg TMA carrier and acidified with concentrated HCl, is spotted on Whatman #1 paper; this is chromatographed for 48 hours with a solution of n-BuOH-12N HCl-H_2O (8:1:1). The paper is then allowed to dry overnight in the chromatography box to evaporate all of the solvent. The dried paper is left on X-ray photo graphic film for 60 hours; the film is then developed. Two well-separated radioactive spots are observed: undecomposed choline chloride and the trimethylamine (TMA) radiolysis product. These are traced with carbon paper from the film onto the paper, and cut accordingly. The pieces of paper are immersed separately in 18 ml of liquid scintillator (toluene containing PPO and POPOP) and the ^{14}C activity counted. The percent of formation of TMA is taken as equivalent to the percent of decomposition. The procedure described above has developed into this form after several modifications since it was used in the early observations of the radiolysis of choline chloride in 1953.

As reported earlier, the choline chloride radiolysis takes several hours at room temperature. Therefore, to speed it up, we have used heating at 50° for 2 hours as post-irradiation treatment. Under these conditions choline chloride's radiolysis does not go beyond about 12%. Possible explanation for this "saturation" of radiolysis are given in the next chapter.

Effect of prior thermal treatment. A few milligrams of choline-methyl-^{14}C chloride were sealed into Pyrex tubes after the tubes and contents had been dried at 100° and 10^{-4} torr for 1 hour. After the sealing, some of the tubes were given no further thermal treatment; others were heated at 70, 100, or 150° for varying periods of time. All tubes were then subjected to 3 Mrads of γ-rays in a ^{60}Co source. The post-irradiation treatment consisted of keeping the tubes at -78° (control), or heating at 50° for either 20 or 120 min.

Effects of added electron-accepting gases. The effects of the four electron-accepting gases, O_2, SF_6, N_2O, and I_2, on the α-form's radiolysis were determined as follows. Very finely divided (to maximize surface area) choline-methyl-^{14}C chloride was prepared by the method of rapid precipitation from absolute ethanol solution on the addition of a large excess of cold dry ethyl ether. Pairs of samples were sealed in tubes under vacuum, or under 700 torr of O_2, SF_6, or

N_2O. In the case of the I_2, the choline was exposed to the vapors (<1 torr) for a few minutes before the tube was sealed. The samples were then irradiated as usual. Post-irradiation treatments consisted of heating at 50° for 20 or 120 min.

Effect of doping with potassium iodide. Potassium iodide was dissolved in MeOH and the solution was injected onto a mass of choline chloride crystals under conditions where the methanol rapidly evaporated before any more than a very small fraction of the choline dissolved. The resultant mixture was 1.0% (by weight) KI and 99% choline chloride. It was then transferred into irradiation tubes, dried at 100° for 2 hours, and irradiated as usual.

Effects of added solid electron acceptors and donors. Samples of labeled choline chloride were mixed, before irradiation, with ten times by weight of the electron acceptor, o-chloranil (Aldrich Chemical Co.), or the electron donor, the triphenylmethane dye Brilliant Green (Matheson, Coleman, and Bell). Experiments were also performed in which the o-chloranil and Brilliant Green were added to the choline chloride after, rather than before, the irradiation.

Phototransfer of electrons. Samples of finely divided, γ-irradiated choline chloride were mixed with approximately equal weights of powdered Brilliant Green, cadmium sulfide, or chlorpromazine (Smith, Klein and French Labs), and a small amount of the mixture was sandwiched, in a glove box, between a brass and a quartz disc. The brass disc contained a cylindrical groove of 0.01 inch and a hole in the side to embed a Chromel-Alumel thermocouple. The sandwiched samples were mounted in a chamber, with a quartz window, through which cold nitrogen could be passed. Different temperatures were obtained by varying the flow rate of the nitrogen. The cell was illuminated for 4 hours with light from a 1000-watt, G.E. Model AH-6, high pressure mercury lamp. The distance from lamp to sample was about 18 cm. The lamp has emission only above 200 nm. Experiments were also carried out with unirradiated choline chloride-Brilliant Green mixtures. Longer time illumination, different intensities of illumination (by interposition of neutral density filters), and visible light illumination (by interposition of Corning 1-69 filter) were also done. Brilliant Green and cadmium sulfide have absorptions in the visible, while chlorpromazine has absorption only in the ultraviolet.

^{14}C labeled choline bromide was prepared as reported before, except that the starting material was ^{14}C labeled choline chloride. Phototransfer experiments were also done for γ-irradiated choline bromide-Brilliant Green mistures.

Effect of different crystal sizes. The sensitivity toward γ-irradiation was observed in (a) choline-^{14}C-chloride that had been crystallized slowly from EtOH-Et_2O to give reasonably large crystals (2-3 mm along the c-axis) and (b) samples of very finely divided choline-^{14}C-chloride prepared by very rapid precipitation from an EtOH solution on the fast addition of a large excess of chilled diethyl ether. To avoid the crystal-phase transition at 78°, both these samples were dried at 70°.

Injection of thermal electrons. The experimental set-up is shown schematically in Figure 14. The details of its operation are reported by Lovelock.[27] Samples of choline chloride were exposed to a

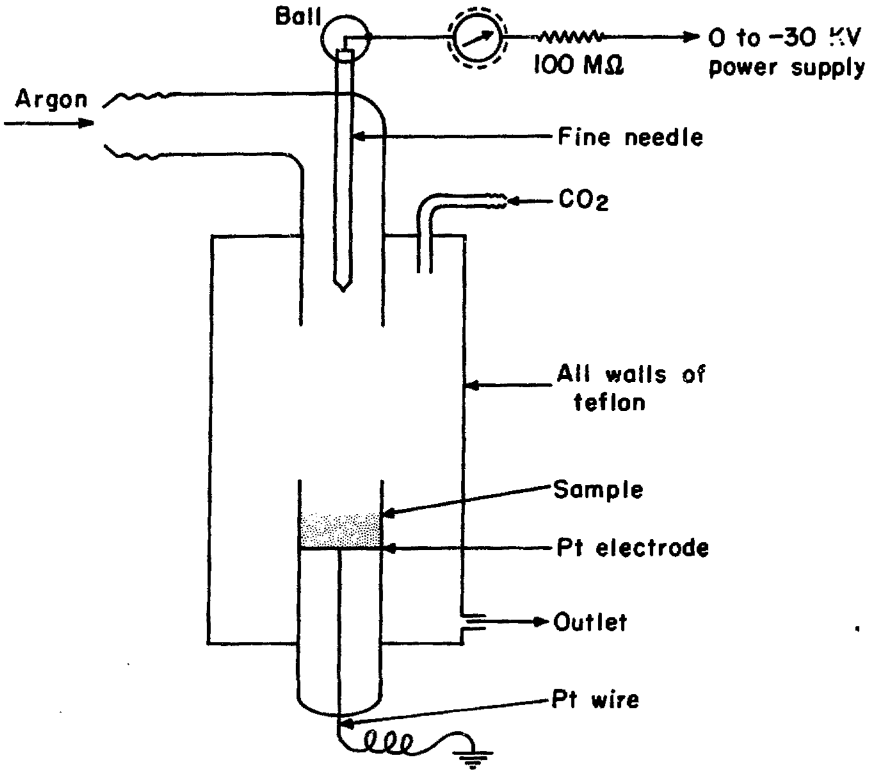

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Figure 14. Apparatus used for the injection of thermal electrons.

current of thermal electrons of about 2 μA for an hour. The voltage varied from 5-8 kV depending on the geometry of the sample and electrodes.

Results and Discussion

A. Thermoluminescence

Irradiation of crystals liberates electrons, some of which become localized in traps. As soom as a high enough temperature is reached, these electrons are released. They can freely migrate in the conduction band and combine with trapped holes, a process that results in photon emission. With increasing temperature, the emission will rise to a peak and then decay as the traps are emptied. The relation between the current and temperature is called a glow curve, the theory of which is discussed by Randall and Wilkins[28] (for constant rate of rise of temperature. Several ways of calculating trap depth energy from these glow curves have been reported.[29-31] We have found this thermal emission for γ-irradiated choline chloride. Two traps were identified. From one of them the electrons are released between -40° and -10° (not shown in Figure 15). Accurate energy determination of this trap was not attempted, because the emptying of the trap affects neither the radical decay nor the radiolysis, The other trap has a peak emission at 67°; this corresponds to an energy depth 2 ± 0.2 eV.[29]

Figure 15 shows the glow curve characteristics of samples irradiated for 1.25 Mrads (curve a) and 15 Mrads (curve b). The higher dose sample has, in addition to the discrete trap sets, a

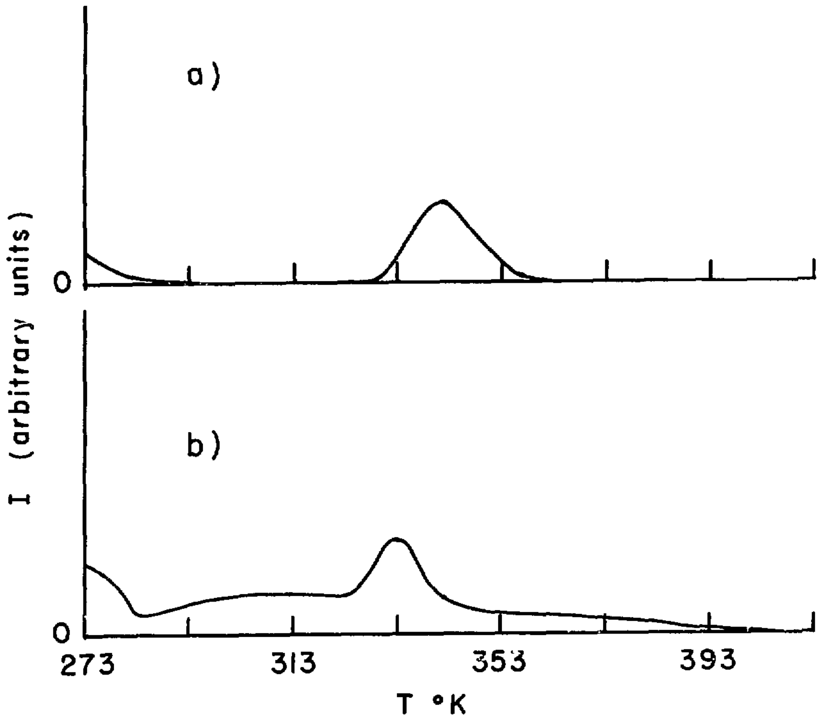

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Figure 15. Thermal emission glow curves of irradiated choline chloride irradiated with (a) 1.25 Mrads and (b) 15 Mrads of γ-rays.

continuous luminescence reflecting a broad spectrum of trap depths, probably due to the defects created during irradiation.

An attempt was made to determine the spectral range of the measured thermal emission. The determination was not 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. We tried to improve the efficiency of current by doping choline chloride with Mn^{++} ions, but this technique did not enhance our light emission, contrary to what has been observed in other systems.[32]

B. Prior thermal treatment

It is reasonable to assume that crystal imperfections in choline chloride constitute potential electron traps and that these are populated with electrons during γ-irradiation. These traps are relatively shallow and, apparently, can be depopulated completely within 2 hours at 50°. This is indicated by the fact that a maximum decomposition of 12-13 percent is attained in that time and it is not exceeded even if the irradiated sample is heated at higher temperatures (but below the 78° transition temperature). This is also supported by thermoluminescence studies. It might be expected that a thermal treatment prior to radiolysis might anneal crystal imperfections that would otherwise serve as electron traps (and, subsequently, as donors). However, the data of Table I indicate that 70° may not be a high enough temperature to achieve significant annealing. Prior thermal treatment at 100° also shows no effect — a possible explanation is that there is extensive

Table I. Effect of Thermal Treatment Prior to γ-Irradiation of Choline Chloride

Prior thermal treatment	Time of post-irradiation heating (50°) 20 min	 120 min
	Percent decomposition[a]	
None	8.2	12.2
2 hr at 70°	8.2	12.3
30 min at 100°	8.2	12.4
8 hr at 100°	8.3	12.2
24 hr at 100°	8.2	12.5
30 min at 150°	6.9	9.4
6 hr at 150°	6.2	8.5
48 hr at 150°	6.5	8.6
144 hr at 150°	5.8	7.8

[a] All analyses are believed accurate to within units of ± 0.2 percent.

reorganization of the crystal structure as the material cools down through the 78° transition temperature. In contrast, prior thermal treatment at 150° leads to a marked decrease in the radiolysis. Whatever happens at this higher temperature appears to survive the "reorganization" of the subsequent cooling through the phase-transition temperature. We believe that the 150° treatment produces a decrease in radiolysis because of slight thermal degradation, leading to species that act as chain terminators or as deep electron traps. In the latter case, these electrons are not detrapped at 50° and thus do not contribute to radiolytic decomposition.

Table II. Effect of Gaseous Ambients

Ambient	Without heating	Time of heating at 50° 20 min	 120 min
		Percent decomposition[a]	
Control (vacuum)	0.2	8.4	12.1
O_2 (700 torr)	0.2	7.9	11.1
SF_6 (700 torr)	0.2	8.0	10.7
N_2O (700 torr)	0.2	8.0	10.6
I_2 (<1 torr)	0.3	4.9	5.6

[a] All analyses are believed accurate to within units of ± 0.2 percent, except for the 120-min I_2 results — the latter are accurate only to within ± 1.0 percent.

C. Electron accepting gases.

The effects of the presence during irradiation and post-irradiation thermal treatment of the added gaseous electron acceptors, O_2, SF_6, N_2O, and I_2, are shown in Table II.

It is apparent that the gaseous electron acceptors have a real, though small, effect in retarding the radiolysis. The I_2 has a particularly large effect. This could arise from any of a number of reasons: (a) it is more efficiently absorbed on the choline chloride (whose surface became visibly yellow on exposure to the I_2 vapor); (b) I_2 acts as both a radical and electron acceptor; and (c) I atoms, formed in small quantity during the radiolysis, also have a large affinity for electrons.

D. Effect of doping with potassium iodide

Doping with 1 percent by weight of KI, before irradiation, was found to reduce the radiolysis from the usual 12 to 8 percent (two separate experiments). The iodine atoms formed during radiolysis apparently compete with radicals for electrons, and thereby inhibit the chain decomposition.

E. Solid electron acceptors and donors

Addition, before irradiation, of an excess (10:1 by weight) of the powdered electron acceptor, o-chloranil, to finely divided choline chloride was found to retard the latter's γ-radiolysis by at least 0 percent (e.g., a measured 10.8% decomposition under conditions that give 12% decomposition for the pure compound). In contrast, a similar addition of the electron donor, Brilliant Green, led to a 7 percent increase in the decomposition. These results appear to support strongly the notion of an important role for free electrons in the radiolysis mechanism. However, it was found that addition of either of these compounds <u>after</u> irradiation produced no obserable effect, <u>i.e.</u>, the radiolysis was neither advanced nor retarded. It appears that the effects observed on addition before irradiation are due to radiolysis products of the acceptors or the donors, rather than to the intact compounds. Such radiolysis products may both retain the overall electron acceptor or donor characteristics of the added parent compound, and, in addition, may have a much higher diffusion rate, permitting a greater effect on the radiolysis.

F. Phototransfer of electrons

If electrons are participating in the chain decomposition, we should be able to observe radiolysis (even at temperatures too low for thermal detrapping of electrons) by phototransferring electrons from an external electron donor such as Brilliant Green,[33] cadmium sulfide, or chlorpromazine.[34] At -40°, even though the phototransfer agent, Brilliant Green, is presumably providing electrons, the radiolysis chain cannot propagate (Table III). However, somewhere between -40° and 12° the chain can propagate when the electrons are made available, owing to higher mobility of the energy-rich, chain-propagating species, or to increased internal energy in a choline cation. Because strong illumination was used, it was possible that heat, rather than photoelectrons, caused the increased radiolysis. However, exposure of the choline chloride-Brilliant Green mixtures to different rates of AH-6 illuminations (by using neutral density filters giving one-fourth photon flux), but to the same total number of photons, gave the same amounts of radiolysis. Evidently, heat plays no role in the Brilliant Green enhanced radiolysis; otherwise the temperature of the sample exposed to a higher photon flux would have been higher than that of the sample exposed to a lower photon flux. This difference in temperatures would have caused different amounts of radiolysis. In the absence of the dye the origin of free electrons is probably thermally-depopulating traps. We have also tried experiments in which γ-irradiated choline chloride-Brilliant Green mixtures were illuminated for 48 hours. The radiolysis obtained was still about 12%. The radiolysis of samples irradiated for longer times and heated also for longer

Table III. Radiolysis of Choline Induced by Phototransfer of Electron

Temperature (approx.) deg.	Percent decomposition						
	γ-irradiated choline chloride mixed with Brilliant Green (1:1)		γ-irradiated choline chloride mixed with cadmium sulfide (1:1)		γ-irradiated choline chloride mixed with chlorpromazine (1:1)		γ-irradiated choline chloride illum. 4 hrs in absence of photodonors
	Illum. 4 hrs	Dark 4 hrs	Illum. 4 hrs	Dark 4 hrs	Illum. 4 hrs	Dark 4 hrs	
-120	1.5±0.2	1.5±0.2[b]					1.0±0.2
-40	1.8±0.2	1.6±0.2[b]					1.6±0.2
12	10.5±0.8	2.0±0.2[b]			6.0±0.2	2.0±0.2	2.1±0.2
12 (with 1-69 filter[c])	9.3±0.4	2.0±0.2[b]					
30	12.0±0.8	5.0±0.1	8.5±0.5	5.5±0.5			5.0±0.5
30 (with 1-69 filter[c])	11.7±0.5	5.0±0.5	7.8±0.2	5.0±0.5			

[a] All these data are averages of at least four analyses.

[b] The 1.5-2% decomposition represents the radiolysis that occurs during the brief period of handling at room temperature in the dry box.

[c] Restricts illuminating light to the 400-800 nm range.

times also saturates at about 12%. There is also no icrease of the radiolysis (beyond 12%), if the illuminated mixture is heated at 50° after photoelectron transfer has taken place. This saturation radiolysis behavior has also been reported by Lindblom et al.[3] The explanation seems to lie in strains developing in choline crystals due to extensive damage, which are discussed in the next chapter.

The other photodonors, cadmium sulfide and chlorpromazine, also show the effects of enhancing the radiolysis by phototransferring electrons. The enhancement is less, probably due to a lower quantum yield of electrons from cadmium sulfide and chlorpromazine. The Brilliant Green is known to be a dye with very high quantum yield.[33]

Phototransfer experiments done with mixtures of γ-irradiated choline bromide and Brilliant Green also gave enhanced radiolysis upon illumination.

When unirradiated choline chloride-Brilliant Green mixtures were used, the radiolysis obtained by illuminating the mixture was the same (approximately 0.2%) as that for mixtures kept in the dark. This suggests that radicals and electrons are both necessary for the radiolysis to occur, probably a radical-electron interaction leading to the formation of highly excited species, which participate in a self-propagating chain reaction involving choline chloride.

From our thermoluminescence results we conclude that the shallow traps are at least as populated as the deep traps. However, both the radiolysis and the radical decay are neglibible in the temperature range (up to about 0°) where the shallow traps are depopulated. A resonable 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. As reported earlier, the ethanol radical decay was found to be extremely slow for temperatures below 10°. Since we know from our thermoluminescence studies that electrons are released below 10°, the conclusion is that the ethanol radicals are not reacting wiht these electrons. These observations may result from a preferential reaction of the detrapped electrons with trimethylamine radicals present.

G. Crystal size

It was found that large, slowly grown crystals of choline chloride show a significantly decreased radiolysis in comparison with the rapidly precipitated compound that had the same (usual) radiation treatment.

Although no significant diminution of radiolysis was observed on 20 min. of post-thermal treatment at 50°, 2 hours at the same temperature resulted in 10.0 and 9.9% decomposition (two experiments) for the larger crystals and 13.5 and 13.3% decomposition for the finely divided material. This is probably due to a lower density of defects in the large crystals and, consequently, a smaller number of donors are formed by the γ-radiation. Similar results in the case of choline chloride were reported by Lemmon and Soltysik[35] and for succinic acid by Miyazaki et al.[36]

H. Effect of thermal electrons

In our ESR work we did not see any signal from trapped electrons. One of the reasons could have been that the signal might be masked by a large signal from the ethanol radicals. We did not see any ESR signal from unirradiated choline chloride that was subjected to the thermal electrons. Even a small signal due to trapped electrons could have been seen as we have no ethanol radicals in unirradiated choline chloride. This may be due to a very small concentration of trapped electrons, or the spin lattice relaxation time is too short to permit us to see the signal. We also looked for thermoluminescence in the thermal-electron exposed samples. We were without success —— suggesting that indeed there are, if any at all, very few traps populated.

A sample of choline chloride which was illuminated by vacuum UV for 2 hours at temperature below 0° was subjected to the thermal electron injection at room temperature for 2 hours. The vacuum UV illumination produces ethanol radicals and causes radiolysis (see later). A control was also illuminated by UV, but not subjected to the electrons. The one subjected to the electrons gave a radiolysis of 0.35 percent compared to the control value of 0.15 percent. Another set of samples were treated just as in the previous experiment except that they were further heated at 50° for 2 hours. The radiolysis for electron-injected samples was 0.80 percent compared to 0.45 percent for controls. In contrast with γ-irradiated samples, we were unable to find any effect of subsequent thermal electron-injection, probably due to the much larger radiolysis in the γ-irradiated samples. The radical decay in these samples was also the same regardless of later exposure to electrons.

The observations suggest that thermal electrons do increase radiolysis, although the effect is rather small. This may be because the concentration of thermal electrons interacting with choline chloride is small.

Some of the results presented here have been published.[23, 37]

Conclusion

From the experiments described here it seems that the radiolysis of choline chloride proceeds as follows: Upon γ-irradiation of choline chloride at low temperatures, radicals are formed and electrons are also trapped. Upon warming, these electrons are released, and interact with the radicals to form some excited species that participate in self-propagating chains. The acceptors will compete for these electrons and thereby retard the radiolysis, while donors will increase the density of free electrons and so enhance the radiolysis. A detailed mechanism to account for these results is proposed in the last chapter.

CHAPTER IV

FURTHER INVESTIGATIONS INVOLVING RADICALS AND ELECTRONS

It has been proposed in the previous chapters that both ethanol radicals and electrons participate in the radiolysis mechanism of crystalline choline chloride. In what follows, experiments involving both the radicals and the electrons will be presented.

A. Effect of free electrons on the radical decay.

Unlabeled choline chloride, in Pyrex tubes sealed under vacuum, were γ-irradiated at -196° for 1 hour (5 Mrads) by the ^{60}Co γ-ray source. The irradiated choline chloride was thoroughly mixed with powdered Brilliant Green, approximately in the ratio of 1:1 by weight, in a dry box at room temperature. Approximately 50 mg portions of this mixture were placed in quartz tubes, which were then sealed under vacuum (10^{-4} torr). The entire operation took about 15 min. The sample was placed in the ESR cavity and the ethanol radical decay kinetics were investigated by locking the ESR spectrometer at the magnetic field of the most intense peak of the ethanol radical. The kinetics were followed as a function of illumination of the sample in the visible-light region of a 450-watt Xenon lamp by interposing Corning 1-69 (300-800 nm) and 3-69 (510-3500 nm) filters. The sample was maintained at 12°, where the radical decay in the dark is known to be small, at all times, both during illumination and in the dark. The lamp was kept at a distance of 15 cm from the sample (as close to the cavity as possible, and with optimal focusing).

If the radical-electron interactions are the only interactions responsible for the radical decay, then

$$-\frac{dR}{dt} = kR[e^-], \qquad [e^-] = -\frac{dR/dt}{kR}$$

where k is the rate constant, R is the radical concentration, $[e^-]$ is the electron concentration, and $-\frac{dR}{dt}$ is the rate of decay of the radicals. Therefore

$$\frac{[e^-]\ \text{illum}}{[e^-]\ \text{dark}} = \frac{\left[\frac{1}{R}\frac{dR}{dt}\right]\text{illum}}{\left[\frac{1}{R}\frac{dR}{dt}\right]\text{dark}} .$$

The radical decay of the choline chloride-Brilliant Green mixture upon illumination and dark is shown in Figure 16. From the data the ratio of the electron concentration for illumination/the electron concentration for dark comes out to be approximately 3. We attribute this enhanced electron concentration in the case of the illuminated sample (or the same thing as enhanced radical decay) to the electrons donated by the dye. It should be mentioned that the radical decay upon illumination by visible light of pure irradiated choline chloride is identical to the radical decay of choline chloride kept in dark at the same temperature. As we have mentioned before, at 12° electron detrapping is small (the shallow traps would have depopulated already during room temperature handling), leaving the number of electrons in the traps virtually unchanged, the radical decay will follow first-order kinetics. Also, during illumination, the number of electrons donated by the dye will remain constant and therefore the radical decay during illumination should also follow the first order kinetics. The plots of the logs of the radical concentrations against time (done for 42 min.) were found to be

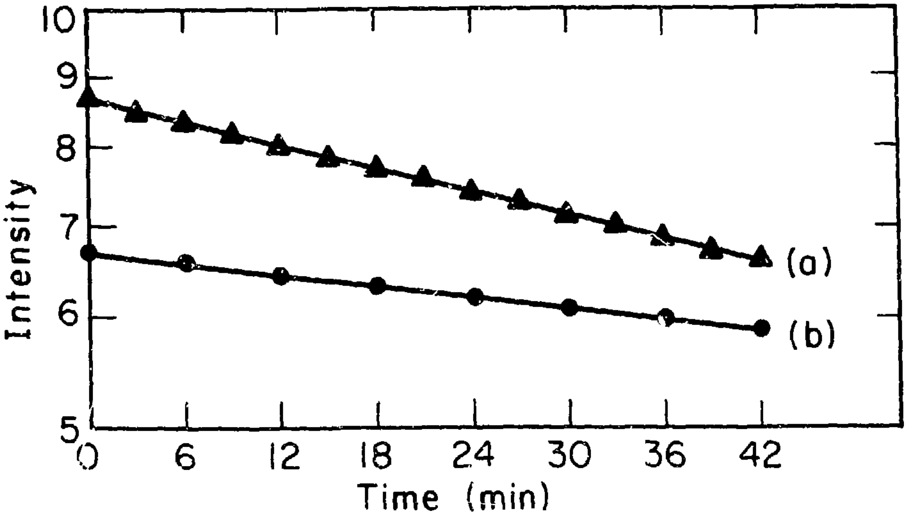

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Figure 16. The radical decay in a mixture of choline chloride and Brilliant Green (1:1) at 12°: (a) Illumination with visible light. (b) No illumination.

straight lines for both the illuminated and the dark cases, as we have seen earlier in Figure 16.

Additional evidence was obtained for the participation of electrons in the radical decay. We studied the ethanol radical decay kinetics for two samples (no Brilliant Green present) —— one was irradiated with 1.25 Mrads and the second was irradiated with 15 Mrads. The decay of the radical signal at 50° 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 in the "higher dose" samples was lower than the concentration of the radicals in the "lower dose". Simultaneous studies of the thermal emissions of the samples irradiated with 15- and 1.25-Mrad 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. It should be mentioned at this point that Lindblom et al.[3] reported that the radical decay obeyed a 3/2 order ($-dR/dt = K[R]^{3/2}$) law. However, insufficient total-dose and time data was used in arriving at this conclusion. We now know that the radical decay does not fit a 3/2 order; neither does it fit 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 slop 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 (Figure 17). The higher initial slop and its more pronounced decrease at higher temperatures can also be explained by faster thermal depopulation of the traps. An additional possibility for explaining the time dependence of the radical decay rate is that the products (mostly trimethylamine hydrochloride and acetaldehyde) are quenchers for the free electrons. (They can not be quenchers for the radicals since, if they were, the radical decay rate would increase with time.)

B. Saturation radiolysis phenomenon.

It has been reported earlier that choline chloride decomposes to an extent of 63 percent upon storage at room temperature for 9 months.[1] Lindblom et al. irradiated the samples over a wide range of doses only to find that the radiolysis saturates at about 12 percent.[3] We have also found in all our experiments that the radiolysis saturates at about 12 percent. In the original observation the radiolysis was due to self-irradiation from ^{14}C β-rays and the dose rate was small, although the sample was being irradiated and decomposing over a long period of time. In our case the dose rate is high and the irradiation is done for a short time. The explanation for this behavior seems to be that the radiolysis products formed react with intermediates in the chain mechanism, thus reducing chain length. In order to test this explanation, certain cyclic experiments were conducted. Aliquots of choline chloride were subjected to repeated cycles of γ-irradiation and heating at 50°. The percent decomposition was compared in each case with

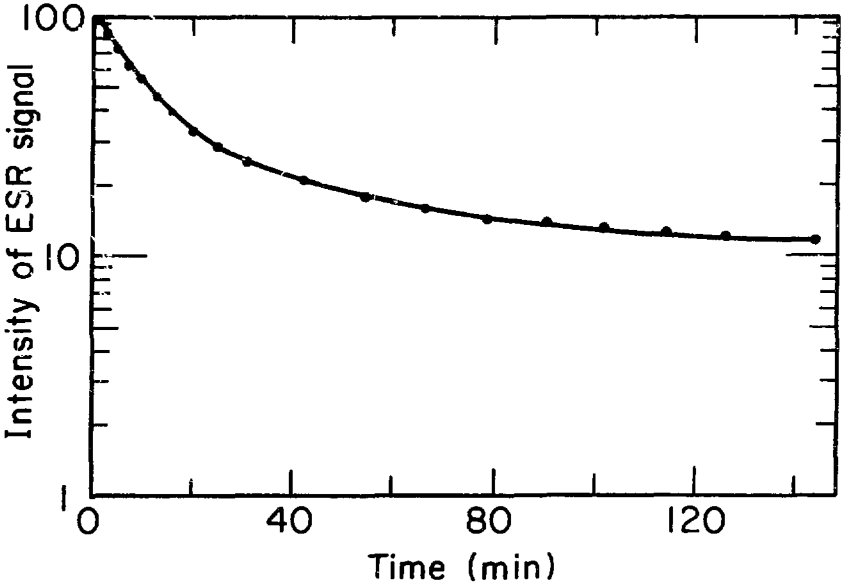

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Figure 17. Radical decay at 50° of the γ-irradiated choline chloride.

that of an aliquot subjected to the same dose of γ-irradiation (in a single irradiation), followed by heating. For example, in a five-cycle experiment the samples were subjected to 1 hour of γ-irradiation followed by heating at 50° for 2 hours; this was repeated five times, and the percent decomposition was compared with that from 5 hours of steady γ-irradiation followed by 10 hours of steady heating at 50°. The latter data are shown in Table IV under the heading "continuous," while the former are shown under the heading "intermittent."

Table IV. Effects of Repeated Cycles of Irradiation and Heating

No. of cycles	Percent decomposition Intermittent	 Continuous
1		12.4 ± 0.5
2	17.6 ± 0.1	12.1 ± 0.3
3	22.7 ± 0.6	12.8 ± 0.2
5	33 3 ± 0.2	13.0 ± 0.3

It appears that no matter how long we irradiate or heat beyond 2 hours, the maximum radiolysis attained in a single cycle does not exceed 13 percent, while the radiolysis in the "intermittent" case is increasing with the number of cycles. A similar observation was made in the case of the phototransfer experiments (reported earlier). It is also interesting to note that almost 50 percent of the decomposition occurs in the first 10 min. of heating at 50° and 90 percent in 60 min. (see next section). All these observations clearly suggest that the chain length diminishes rapidly with time of heating. It seems that at least one of the products of radiolysis is acting as a chain terminator. Experiments have shown that post-irradiation thermal treatment yields lower decomposition in an ambient of acetaldehyde. The experiments were conducted similarly to the experiments with gaseous ambients reported earlier. Choline chloride samples were exposed to the vapors of acetaldehyde at room temperature and they were sealed; the samples were then γ-irradiated at -196° and heated for 2 hours at 50°. The radiolysis obtained was only 6.5 percent (compared to about 12.4 percent for the samples without acetaldehyde). A possible explanation of the saturation radiolysis could be that once all the traps are populated during γ-irradiation, further irradiation may have no effect in promoting radiolysis. But this is unlikely as our thermoluminescence results have showm that the density of trapped electrons in a sample receiving 15 Mrad is at least twice that of the sample receiving 1.25 Mrad. In view of the above observations, we can rationalize our cyclic experiments in the following manner. In the initial stages of heating, a small fraction of the radicals decay via interaction with electrons, with the propagation of long chains. As the concentration of products of radiolysis builds up, the chain lengths diminish. During the later stages of heating, say, beyond 1 hour, the dominant process seems to be the diffusion of acetaldehyde to the surface of the microcrystallites. Consequently, if this heated material is γ-irradiated again, the initial stages of the second post-irradiation thermal treatment would involve much long . chain lengths than the heating during the latter half of the 2 hours period of the first cycle.

(It is also interesting to note that, within the range studied, every cycle subsequent to the first appears to result in an additional 5 percent decomposition.) In short, one obtains a much larger radiolysis via cyclic irradiations and heatings as compared to a single continuous experiment, because relatively longer chain lengths are involved in the former case.

Additional evidence for the reduction of chain lengths as the radiolysis proceeds is obtained by comparing the radical decay kinetics and the radiolysis kinetics. If the decay of radicals is taking place entirely due to the radical-electron interaction and there is no alternative competing mechanism for decay of radicals, then we would expect correspondence between the kinetics of radiolysis and radical decay. What we found, on the contrary, is that the radical decay was faster than the radiolysis. At a temperature of 50° the radical decay half-time is 4.5 min., and that of the radiolysis is 6.0 min. We believe that this lack of correspondence is due mainly to the fact that the chain lengths decrease with increase in decomposition. However, there is also the possibility that a fraction of the radicals are undergoing decay by an alternative mechanism, for example, radical-radical reactions between close neighbors (see below).

C. Effect of dose and temperature on radiolysis kinetics.

Approximately 5 mg samples of methyl-^{14}C-labeled choline chloride were vacuum sealed in 5-mm Pyrex tubes. The sealed tubes were γ-irradiated, receiving a dose of 1.25, 5.0 or 15.0 Mrads at -196°. The irradiated samples were than heated at any one of three temperatures, 22.5°, 50°, or 71°, in a constant temperature oil bath, for different lengths of time. The radiolysis in each sample was then determined.

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 hours) storage is less for a 15-Mrad sample than for a 1.25-Mrad sample (Figure 18). At 50° (see Figure 19), the 1.25-Mrad sample will probably give a higher final radiolysis than the 5- and 15-Mrad samples (the latter have reached the "saturation radiolysis" of about 13-16 percent, while the 1.25-Mrad 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 Mrads we have observed as much as 0.3 percent 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). The products were probably polymers as the ^{14}C-activity of these products was found at the paper-chromatographic origin (where the solution is spotted). Such unusual products may be responsible for the diminished radiolysis.

However, as the data of Figure 19 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

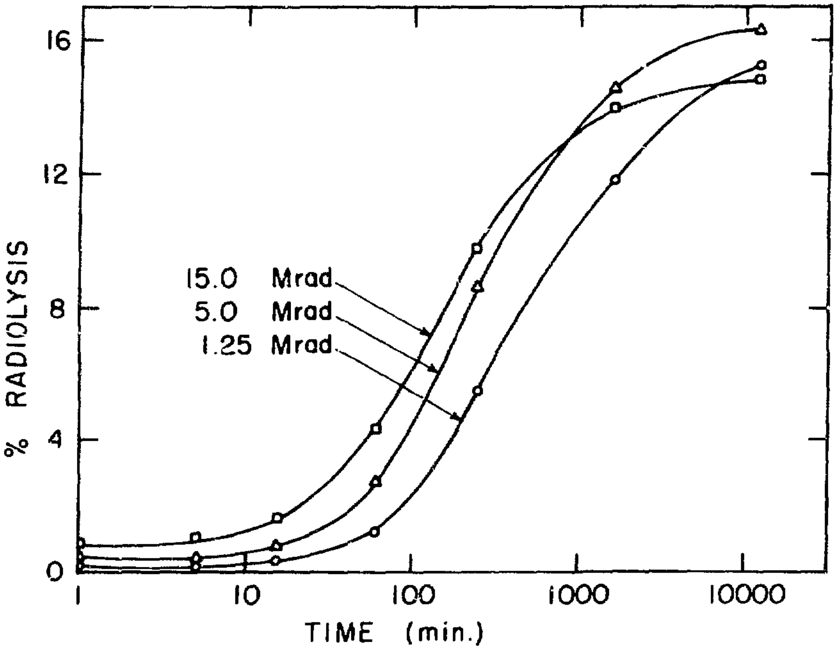

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Figure 18. Radiolysis of choline chloride at 22.5° as a function of total radiation dose and storage time.

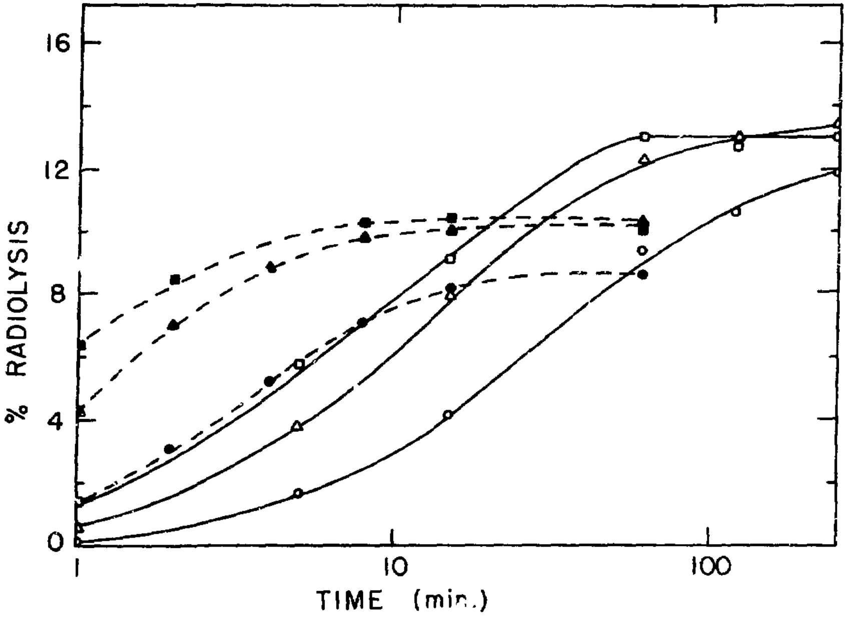

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Figure 19. Radiolysis of choline chloride (50° and 71°) at different total doses: (o, △, □) 1.25, 5.0, and 15.0 Mrads, respectively at 50°; (●, ▲, ■) 1.25, 5.0, and 15.0 Mrads, respectively at 71°.

to the usual values of 13-16%. The reason is probably the occurence 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 electron 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°). These other processes, whose mechanisms we do not yet know, also make the kinetic analysis very complicated. 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 V, show clearly that the radiolysis does indeed decrease with increase in temperature.

Table V. Dependence of Choline Chloride Radiolysis on Dose and Post-irradiation Temperature

Temp. (For 100 min.)	Dose (Mrads)	Percent 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

If trimethylamine hydrochloride is heated at 70°, under vacuum, it evaporates slowly. This may offer an alternative explanation for the reduction in radiolysis for post-irradiation heating at higher temperature. But, that this is not so is verified in the following way: Two irradiated choline chloride tubes were heated at 70° for 2 hours and then cooled. From one tube a solid aliquot was dissolved in methanol (normal procedure) while from the other tube all of the sample was dissolved and the tube was thoroughly washed to extract all possible TMA sticking to the walls. The two analyses gave the same radiolysis value of 9 percent.

Shanley and Collin reported an increasing $G_{(-M)}$ value with temperature.[6] Our results show that the $G_{(-M)}$ value falls if the radiolysis is carried out at higher temperature. The discrepancy lies in the fact that they irradiated the samples at high temperature; this permitted the rapid diffusing away (<u>during</u> the irradiation) of the radiolysis products, whose presence inhibits the radiolysis mechanism (see Saturation radiolysis phenomenon).

It may be of great significance that at 74° the radiolysis has only reached about 9 percent. In the β-form, the form which is radiation stable and exists at temperatures above 78°, 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.

So far, we have been unable to prepare (by quick freezing) a sample in the β-form at any temperature below approximately 78°. Nor does there seem any possibility of getting the α-form at some temperature above 78°.

D. Effect of temperature on the radiolysis of choline bromide.

The samples of choline bromide were sealed in vacuum ($< 2 \times 10^{-4}$ torr) in 5-mm O. D. Pyrex tubes. They were irradiated with ^{60}Co γ-rays at -196° for 45 min., for a total dose of 4 Mrads. Different tubes were then heated for 2 hours at 50°, 70°, 85°, and 110° respectively. The radiolysis products were then analyzed using unidirectional paper chromatography. The results are shown in Table VI.

Table VI. Radiolysis of Choline Bromide

Post-irradiation temp.	Time (hours)	Percent Radiolysis
50°	2	6.75, 6.83
70°	2	8.06, 7.95
85°	2	6.27, 6.14
110°	2	1.55, 1.63

It is clear that choline bromide undergoes very small radiolysis at 110°, suggesting that there may be a radiation-stable high-temperature polymorph, quite analogous to the situation with choline chloride. The crystallography to ascertain this possibility has not been done, but conductivity measurements and infrared studies do suggest that there may be a phase transition in choline bromide at 91° (see next chapter). It is also interesting to note that the radiolysis at 85° is less than the radiolysis at 70°. A similar behavior was also found for choline chloride except that the reduction in radiolysis started at a lower temperature. The results can be explained by supposing that deeper traps are populated with electrons during irradiation. In such a case the electrons can be depopulated only at higher temperatures. At these temperatures competitive reactions like radical-radical decay, or electron capture by a hole, may become more important than the radical-electron reactions that are responsible for radiolysis. We have already reported earlier that the radical decay of choline bromide above 25° is slower compared to choline chloride. Also that there is an ESR signal in choline bromide at about 80° (not corresponding to ethanol radicals) that may also be responsible for the reduced radiolysis of the bromide.

E. Kinetics of radiolysis at room temperature.

The data of Figure 19 have been replotted on expanded linear time scale for times up to 4 hours (Figure 20). If the radiolysis products are interfering with chain propagation, then the rate of radiolysis increase should decrease with time, i.e., with increased product formation. It can be seen in the linear plot in Figure 20 that the rate of radiolysis actually increases for some time. This time depends on dose and temperature. For the 1.25-Mrad sample at room temperature, the radiolysis rate appears to increase during the first 4 hours.

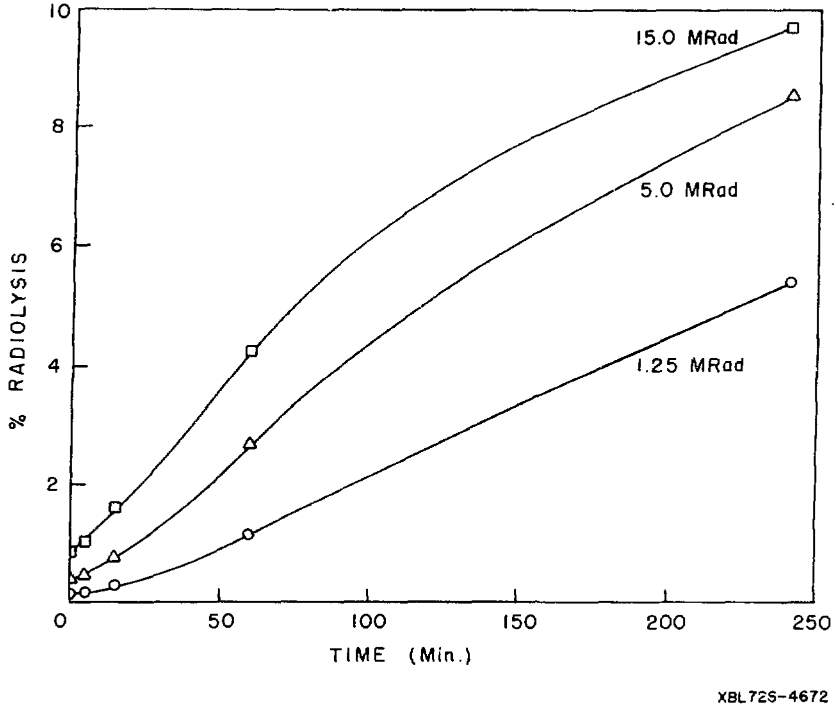

Figure 20. Radiolysis of choline chloride at 22.5°, and different total doses.

During this time the amount of products formed is small and should have no effect on the rate of radiolysis. The increase can be explained on the basis of formation of a radical-electron intermediate. This formation is fast, but the intermediate's reaction with choline chloride is slow (it may be that the intermediate, which would be highly excited energetically, decomposes or is transformed very fast into species A, B, C, etc., and one of them might be responsible for the chain radiolysis of choline chloride):

$$R\cdot + e^- \xrightarrow{k_1} [Re]^-$$

$$[Re]^- \xrightarrow{k_2} A + B + C \qquad\qquad k_1 > k_3$$

$$A + \text{choline} \xrightarrow{k_3} A + \text{products}$$

In such a case there will be a build-up of intermediates to a maximum steady-state value, and the rate of product formation will increase up to this time. The opposing effect of product interference will thereafter become important, finally causing the radiolysis to become so slow that a "saturation radiolysis" is reached.

F. Quantitative radical decay and radiolysis kinetics.

We have reported earlier that attempts to fit our experimental data of radical decay and radiolysis to any simple kinetics have failed. The reason is that the concentration of electrons, $[e^-]$, that are released upon warming could be treated as follows:[28] The probability "p" of electrons released from traps upon warming at any temperature

T is $p = s\ \exp(-E/kT)$, where s is the frequency factor, E is the trap depth, and k is the Boltzmann constant. Therefore the rate of release of trapped electrons is

$$dn/dt = -ns\ \exp(-E/kT) \text{ or } n = n_0\ \exp\{-st\ \exp(-E/kT)\},$$

n and n_0 being the trap density at t and 0 times, or the concentration of electrons released = $n_0 \left(1 - \exp[-st\ \exp(-E/kT)]\right)$, which in itself is a complicated expression. In addition, the radical-radical interactions and electron-hole interactions make the analysis virtually impossible. We thought it would be possible to analyze the experimental data if we could produce either trapped electrons or radicals in choline chloride. The unsuccessful efforts to populate traps by thermal electrons have already been reported. To investigate the possibility of having radicals without trapped electrons in choline chloride we proceeded as follows: The γ-irradiated choline chloride samples were dissolved at -15°, in a cold room, either in dimethylsulfoxide or in dimethylformamide; quartz tubes were filled with the solution, and the solution was frozen at -196° by dipping the tubes in liquid nitrogen. The idea was that once the choline chloride dissolves, the traps would vanish (the traps are only due to crystal imperfections in the solid state), while the radicals may survive in the solution. However, the frozen samples gave no ESR signal, implying that radicals had sufficient mobility to interact with each other, or with the solvent, and decay very fast (before the solution could be frozen). The radiolysis obtained was also very small. Thus our attempts to study the radical decay and the radiolysis kinetics quantitatively were unsuccessful.

G. Absorption properties of γ-irradiated choline chloride.

Radicals are formed and electrons are trapped upon γ-irradiation of crystalline choline chloride, and they may absorb ultraviolet or visible light in regions where there is no absorption by unirradiated choline chloride. We used a Cary Model-14 spectrophotometer (with scattering attachment) for our studies. A small amount of a γ-irradiated sample of choline chloride was placed in an optical grade quartz cell, and unirradiated choline chloride was used for the reference cell. The absorption spectrum recorded is as shown in Figure 21. It seems that there are two absorption bands: one at about 6000 Å and the other at 4400 Å. The 6000 Å absorption is equivalent to an energy of about 2 eV and it seems that this corresponds to an absorption by trapped electrons. Our thermoluminescence data gave 2 eV as the trap depth. The other band at 4400 Å may be due to the absorption of energy by radicals. The absorption bands seem to decay with time, i.e., as the radiolysis proceeds. The results reported here are not very reproducible, probably due to much scattering by the polycrystalline powder. In addition, choline chloride undergoes radiolysis forming trimthylamine hydrocholride and that will perturb the recording of the spectra.

H. Photochemical transformation of ethanol radicals in irradiated choline chloride.

A sample of γ-irradiated choline chloride was sandwiched between brass and quartz discs in a glove-box at room temperature, and illuminated through the quartz window with an AH-6 high pressure mercury

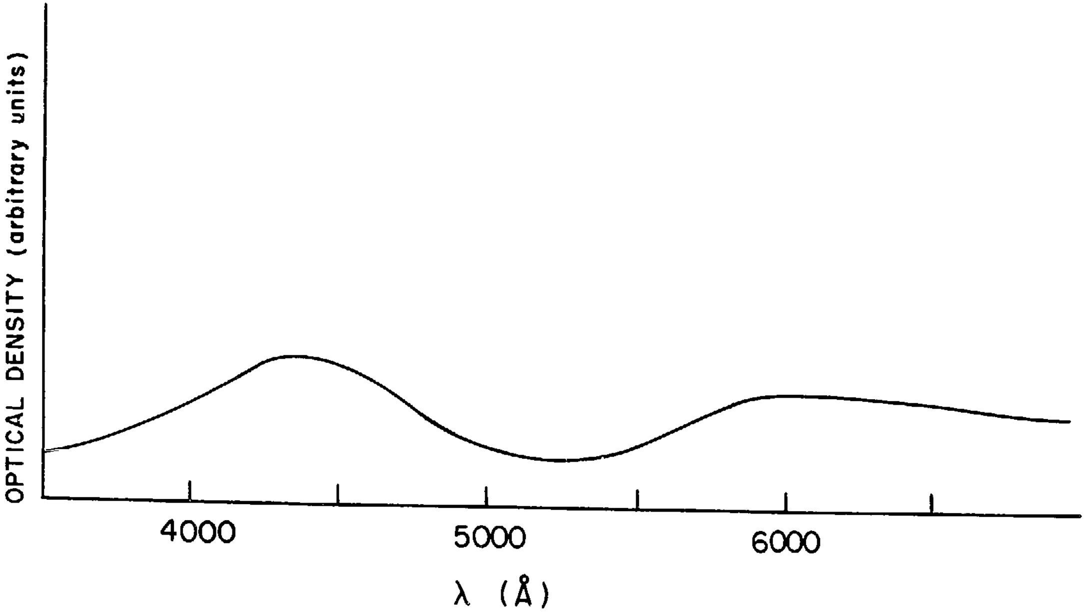

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Figure 21. Optical absorption of γ-irradiated choline chloride.

lamp (emission above 200 nm only) for 4 hours from a distance of about 18 cm. During the illumination the sample was kept at about -20°, and the quartz window was kept free of condensing atmospheric moisture by a stream of room temperature nitrogen. In order to investigate the wavelength dependence of the photochemical transformation of the ethanol radicals, we interposed Corning filters 7-54, 4-71, or 3-69 between the AH-6 lamp and the choline chloride samples. The transmittance of these filters is in the approximate wavelength range 250-400, 350-570, and 530-1000 nm respectively, and is shown in Figure 22. It took approximately 15 min. to prepare the samples for illumination and therefore the controls were also kept at room temperature for 15 min. and at -20° for 4 hours. Similar experiments were done to investigate the effect of photochemical transformation on radiolysis by using methyl-^{14}C-labeled choline chloride. In radiolysis experiments the illuminated and the control samples were given post-illumination thermal treatment at 50° for 90 min. The ESR spectra recording and radiolysis determination were carried out by the usual methods.

ESR spectra of a control, non-illuminated sample and that of an illuminated specimen (no filters interposed) are shown in Figures 23a and 23b respectively. Both spectra were taken at ambient temperature. The concentration of the ethanol radicals is reduced by a factor of about ten during illumination. In addition to the decay, a new radical is formed as a result of the phototransformation of the ethanol radical. The presence of the new radical (superimposed upon the ethanol radical) is shown by the new peak marked "1" in Figure 23b. It is

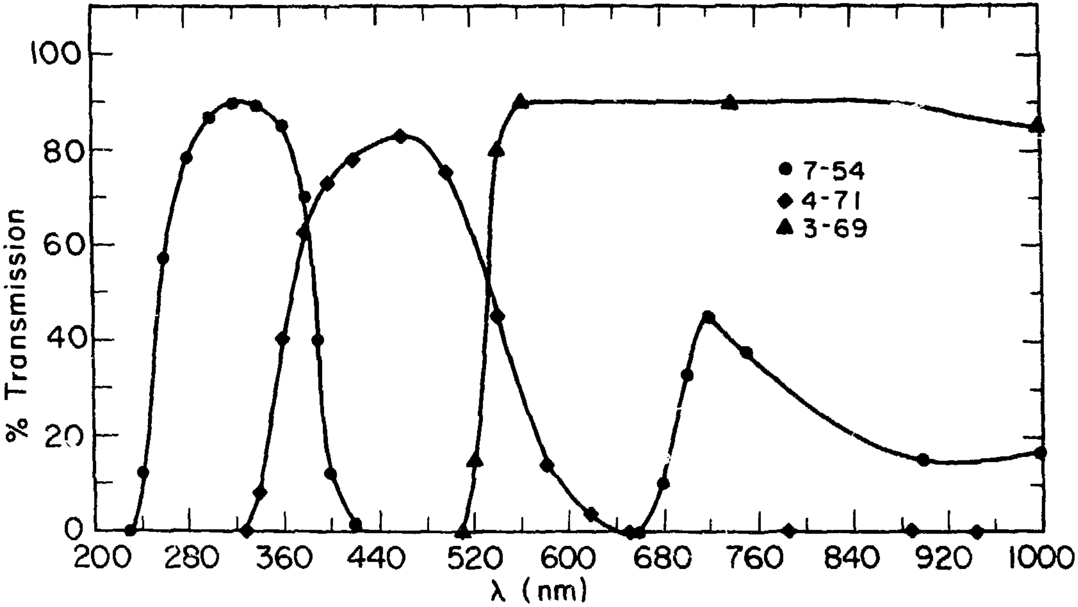

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Figure 22. Transmission characteristics of optical filters.

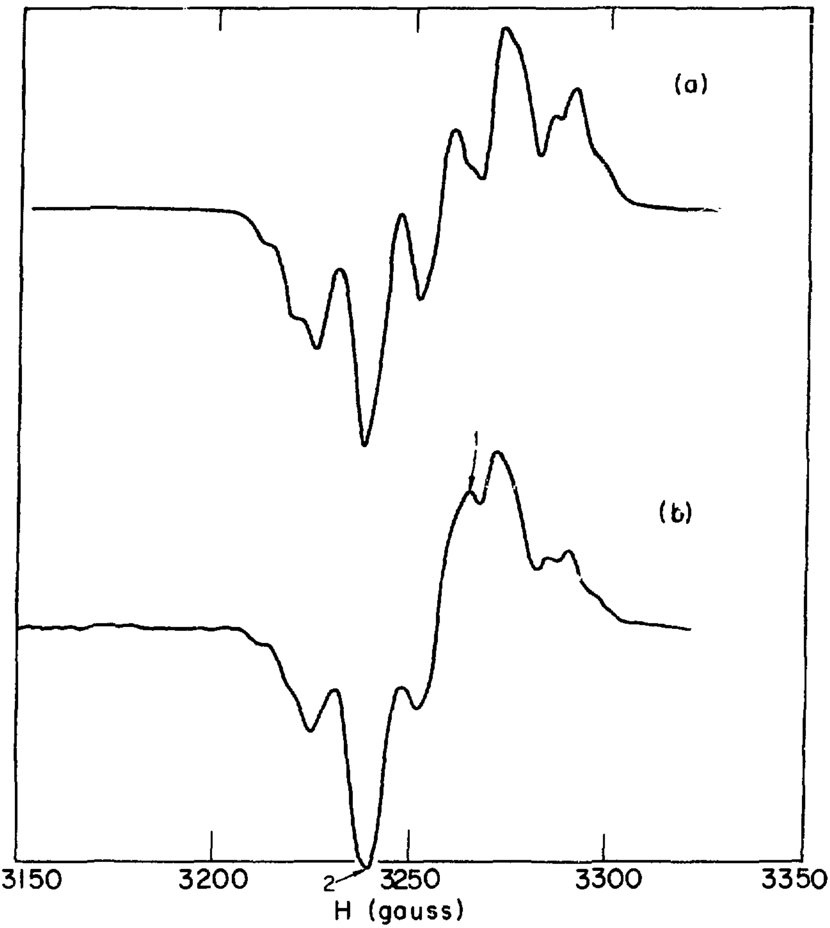

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Figure 23. Phototransformation of the ethanol radicals. (a) ESR spectrum of γ-irradiated, but unilluminated, choline chloride at 22°. (b) ESR spectrum of γ-irradiated and illuminated choline chloride at 22°.

also observed that the peak marked "2" has been shifted to higher fields compared to what it was in the non-illuminated sample (Figure 23a). When the illuminated sample is heated at 70°, the ethanol radical completely decays, and only the photo-transformed radical is observed (Figure 24). The heating of the control sample at 70° leads to the loss of all radical signal. The new radical is relatively stable and the signal further decays, over 16 hours at 70°, to about 2/3 of the original value.

According to our earlier proposal free electrons interact with ethanol radicals to form reactive species that participate in a self-propagating chain mechanism. It follows that if the concentration of ethanol radicals was reduced by photo-decay at low temperature (where radiolytic decomposition does not take place) then the decomposition of the compound by post-illumination thermal treatment would be diminished. This is indeed what happens. We have found that irradiated and illuminated samples (4 hours at -20°) of choline chloride are approximately 4.8 percent decomposed on subsequent thermal treatment (90 min. at 50°). On the other hand, samples treated in exactly the same way (except for illumination) showed approximately 7.6 percent decomposition. The photo treatment reduces both the ethanol radical concentration and the subsequent radiolysis. Therefore, the involvement of the ethanol radicals in the radiolysis has been directly observed.

We found no effect on the radical decay or the formation of new radicals in the cases of the 4-71 (350-570 nm) and 3-69 (510-3500 nm) filter interposition. The use of the 7-54 (250-400 nm) filter led to a reduction of the ethanol radical's intensity by a factor of three (the

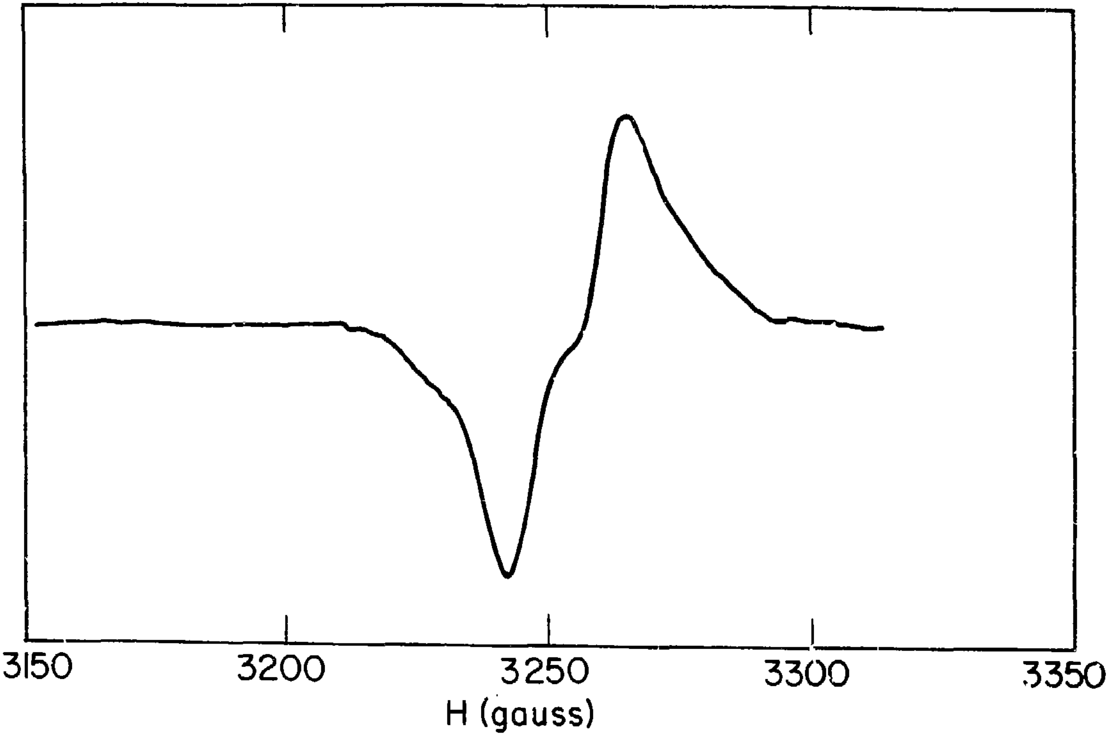

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Figure 24. ESR spectrum of γ-irradiated and illuminated choline chloride at 22°, after being heated at 70° for 2 hr.

unfiltered illumination gave a reduction of a factor of ten), and the new radical's intensity was about the same as in the unfiltered illumination. This suggests that the decay of the ethanol radicals takes place within the 200-350 nm range (the shorter wavelengths being more effective), while the formation of the new radical takes place between 250 and 350 nm.

The photo-detrapping of electrons is expected to occur in longer wavelength regions —— about 2 eV or 600 nm —— as indicated by our thermoluminescence studies reported earlier. Therefore, the radical decay on illumination appears not to be due to interaction with photo-detrapped electrons. In fact, there is no difference in the radiolysis of the samples (a) illuminated with > 400 nm (Corning 3-73 filter) at -20° and (b) kept in dark at -20°. This is surprising and we do not know why there is no photo-detrapping of electrons. A possible explanation may be that there is a large amount of scattering by polycrystalline samples and thus enough light does not reach all the sample.

CHAPTER V

ELECTRICAL CONDUCTIVITY AND INFRARED STUDIES OF CHOLINE CHLORIDE AND ITS ANALOGS

Since free electrons are playing an important role in the radiolysis of cholinechloride, the study of the migration of electrons (conductivity behavior) in its matrix may provide us with some valuable information.

Most crystalline organic solids studied thus far have been shown to be semiconductors which follow the conductivity-temperature relationship shown below.[38]

$$\sigma_T = \sigma_\infty \exp(-E/2kT)$$

where σ_T is the specific conductivity at temperature T, σ_∞ is the specific conductivity at infinite temperature (also called preexponential factor), k is the Boltzmann constant, and E is the energy gap between the valence and the conduction bands. E can be determined by the measurement of the conductivity as a function of temperature. We have also studied the conductivity behavior of the radiation resistant (β) form of the choline chloride and extended studies to some other choline analogs. The conductivity studies were done under the influence of dc voltages and also with electrodeless microwave techniques.

We have also investigated the infrared absorption by choline chloride and some of its deuterated and undeuterated analogs, in order to shed some light on the specificity of the radiation sensitivity of the α-form of choline chloride.

A. dc conductivity.

dc conductivity measurements on choline chloride made on both pellets and powders in an evacuated ($\simeq 10^{-5}$ torr) conductivity cell. Details of the apparatus and its use have been described by Eley and

Pacini and shown in Figure 25.[39] The pellets were made in a hydraulic press under 10,000 kg/cm^2 pressure using a Beckman KBr evacuable die. The current measurements were done on a vibrating reed electrometer obtained from the Applied Physics Corp. (Cary Model-401).

The conductivity data for the pelleted choline chloride are shown in Figure 26. The powder (compressed to about 40 kg/cm^2 between the electrodes) shows, in all respects, conductivity behavior similar to that of the pelleted material. There is a sharp increase in conductivity around 78°, which corresponds to the temperature of the phase transition. The conductivity increases by about four orders of magnitude. The evidence for the phase transition, on the basis of the crystallographic and density measurements has already been reported earlier.[5-8]

The conductivity in the β-form is high enough to cause its decomposition, even though choline chloride is thermally stable up to 200°. This decomposition behavior is shown by the pellet 1 data of Figure 26 (in addition, the pellet was visibly charred). Pellet 2 was not heated beyond 90°, and was subjected to five reproducible cycles of heating and cooling (only one cycle is shown in the figure). Such sharp and large changes in conductivity at the phase transition have not hitherto been reported. An increase of an order of magnitude was reported in chlorpromazine,[40] but we also studied this compound and found that this increase is observed only if the conductivity measurements are done without evacuation, <u>i.e.</u>, the effect is due to the presence of adsorbed atmospheric moisture. Wihksne and Newkirk have also

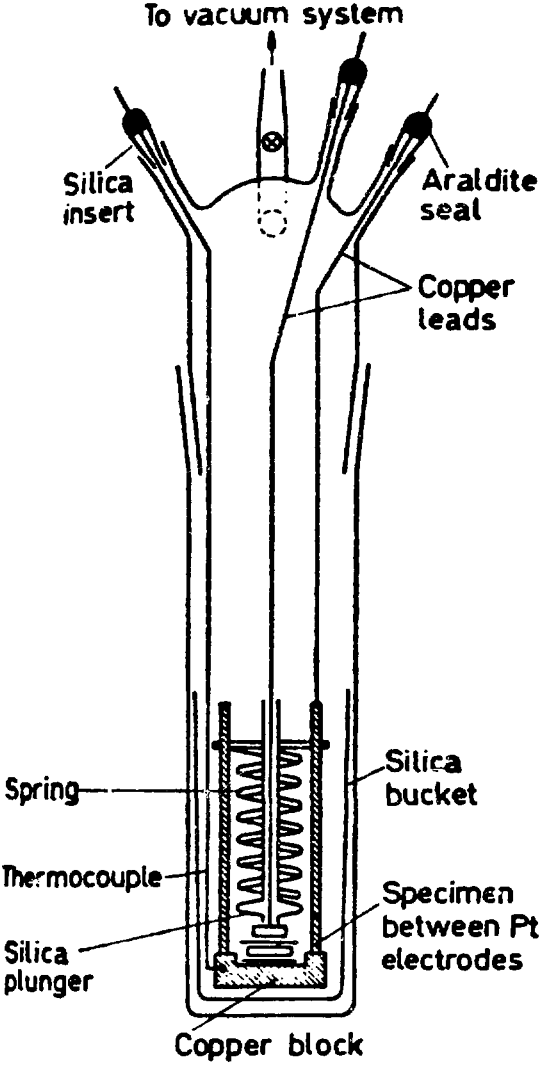

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Figure 25. Apparatus for measuring D.C. conductivity.

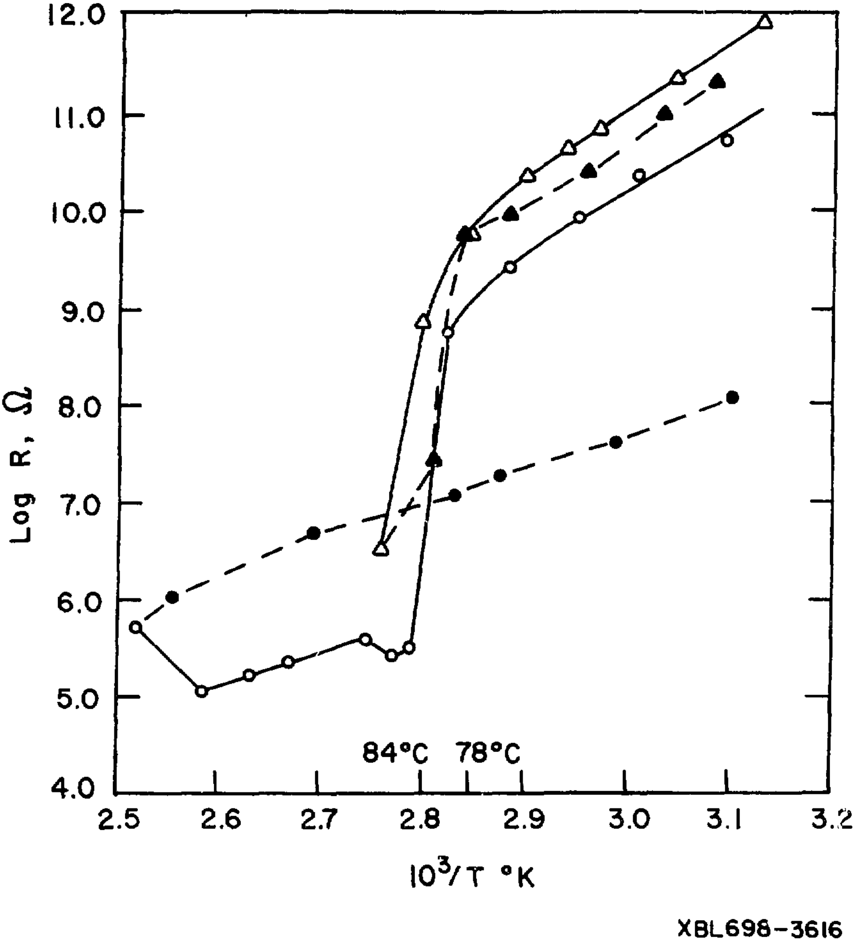

Figure 26. Electrical conductivity of choline chloride: (o) pellet 1, heating; (●) pellet 1, cooling; (Δ) pellet 2, heating; (▲) pellet 2, cooling.

reported large changes in conductivity of metal-free phtalocyanine, but the decrease is non-reversible (actually the phase transformation is non-reversible), and takes place over a large temperature range.[41] Conductivity in the α-form appears to be electronic (see below). Ohm's Law is obeyed, i.e., the voltage-current plot is a straight line. The measurements for this voltage-current plot were done to a temperature of 70° and for voltages up to 22.5 V, corresponding to an electric field of about 300 volts/cm. The current reaches its final value within a few seconds of the application of the voltage. On the contrary, in the β-form, i.e., above the 78° transition point, any increase in applied voltage results in a geometric increase of current. For example, doubling the voltage results in a tenfold increase of current. Such instances have been encountered only in systems where there are strong indications of protonic conductivity.[42] In addition to this non-ohmic behavior, a marked polarization is observed, i.e., the current slowly decreases with time (e.g., from 8μA to 4.6 μA in 25 min.) and reaches a steady value after an hour, or even longer. Relaxation times of such duration are characteristic of ionic conductivity as opposed to electronic conductivity where the relaxation times are of the order of milliseconds to seconds.[43] Besides, on turning off the applied voltage, we noted a residual voltage (100 mV to 1 volt) with sign opposite to that of the initially applied voltage. This, again, could be due to the overvoltage characteristic of systems displaying ionic conductivity.

Collins has inferred, from crystallographic symmetry considerations, that the face-centered cubic form (β-form) has a highly disordered structure and has sufficient room for spherical rotation about a number of equilibrium positions. Therefore, it seems that the conductivity in the β-form is probably protonic. Such conductivity necessarily means easy intermolecular transfers of protons through hydrogen bonds. There is crystallographic evidence for hydrogen bonds[7,8] and also evidence for some intermolecular hydrogen transfers in choline chloride.[9] The free rotation of choline ion in the β-form would also facilitate the intermolecular transfer of protons. It is possible that these protons might be responsible for the radiation-resistant nature of the β-form, if we postulate that the protons react with electrons to give hydrogen atoms which in turn react with the ethanol radicals as follows:

$$\text{(a)}\quad \cdot CH_2CH_2OH + H^{\cdot} \longrightarrow CH_3CH_2OH$$

$$\text{or}\qquad \text{(b)}\quad \cdot CH_2CH_2OH + H^{\cdot} \longrightarrow CH_3CHO + H_2$$

In this way, the initiation of chain decomposition, resulting from an electron-radical interaction, is prevented. It is possible to demonstrate protonic conductivity by detecting the evolution of hydrogen at the cathod,[45] and by the dc Hall effect.[46] But, due to experimental problems associated with choline chloride's hygroscopicity, we have not done it. However, we tried the microwave Hall measurements for the sign of charge carriers (see below). The sharp increase in the conductivity at 78° could be due either to a sudden increase in the number of charge carriers or to a sharp change in the mobility of the majority carriers. Protonic conductivity in solids is not very common, but has been reported.[45, 47]

As pointed out earlier, the sharp increase in conductivity of choline chloride corresponds to a phase transition. However, the crystallographic work has not been done at any temperature other than room temperature for choline bromide and iodide, and none at all for the chloro analog, $[(CH_3)_3NCH_2CH_2Cl]^+Cl^-$. The dc conductivity data (powders compressed to 40 kg/cm^2) obtained for these compounds are shown in Figure 27. The band energies, E, together with the temperatue at which sharp changes in conductivity take place, have been tabulated in Table VII.

Thus, though no independent investigations of phase transformation in choline bromide, choline iodide, or the chloro analog have been made, it seems very likely that these choline analogs display different crystal structure beyond the transition point. It should be noted that this is not characteristic of quaternary ammonium salts since tetramethyl ammonium chloride shows no such behavior. Similar to choline chloride, these analogs also undergo rapid electrolysis under low electric fields (30 V/cm) when they are in the high temperature form. They also display polarization effects and non-ohmic behavior, suggesting a protonic conductivity, just as in choline chloride, in their high temperature polymorphs.

There is, as yet, no direct relationship between radiation sensitivity and electrical conductivity. Both choline chloride and bromide are much more radiation sensitive at temperatures below their transition points while the iodide and the chloro analog are not sensitive to radiation. In the chloride and bromide it is possible to attribute the

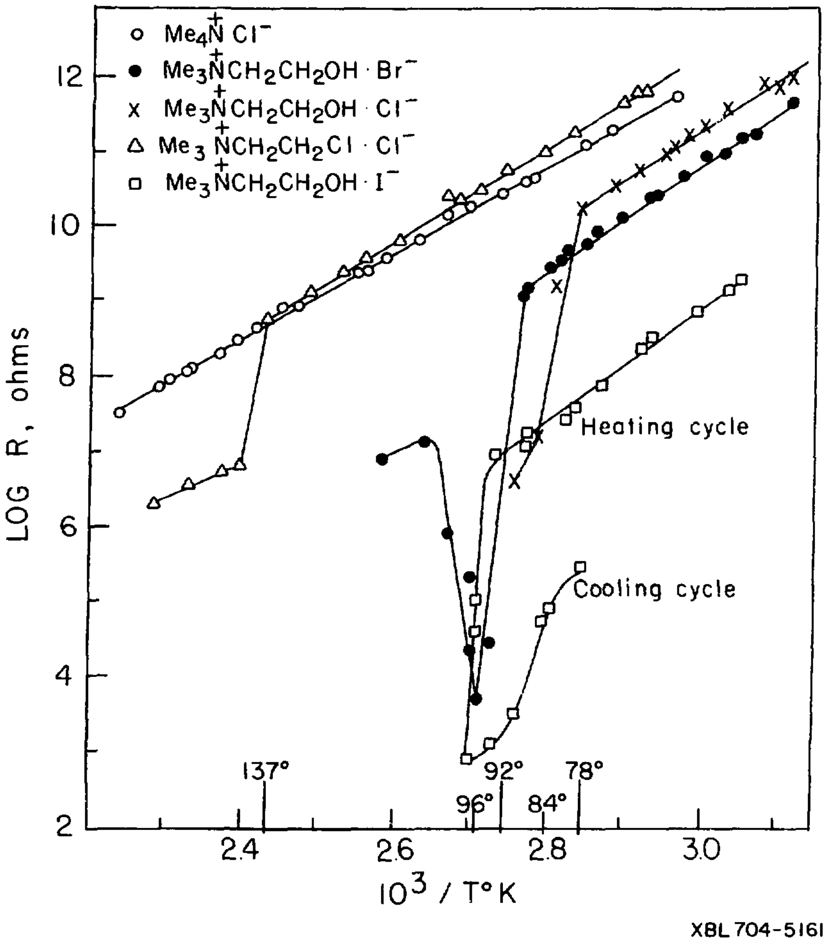

Figure 27. Electrical conductivity of choline analogs.

lack of radiation sensitivity above the transition temperature to protonic mobility, while the same is not necessarily true for the chloro analog and the iodide. In the latter two cases, further physical data (crystal structure, etc.) are necessary before one can speculate on their lack of radiation sensitivity.

Table VII. Semiconduction band-gap energies and transition temperatures of choline chloride and its analogs

No.	Substance[a]	E, eV	Transition temperature °C
I	$[Me_3NCH_2CH_2OH]^+Cl^-$	2.7	78
II	$[Me_3NCH_2CH_2OH]^+Br^-$	2.7	91
III	$[Me_3NCH_2CH_2OH]^+I^-$	3.0	94
IV	$[Me_3NCH_2CH_2Cl]^+Cl^-$	2.5	137
V	$Me_4\overset{+}{N}\ Cl^-$	2.3	None

[a] Me stands for (CH_3) group

To find out if the precipitation procedure of choline chloride has any effect on its radiolysis, we used petroleum ether (b.p. 60-80°) in place of diethyl ether as the precipitating agent to get choline chloride out of ethanol solution. We noticed that the choline chloride's hygroscopicity was far less than we encountered in the diethyl ether precipitated samples. We studied its radiolysis behavior and found that it decomposes as much as the conventional choline chloride (the samples were dried on the vacuum line at 70°, rather than 100°, for 2 hours). The ESR spectrum of these samples was also identical to the ones from diethyl ether precipitated choline chloride. However, the conductivity behavior is surprisingly different. The resistance vs. temperature plot of the petroleum-ether precipitated choline chloride is shown in Figure 28. Here, the choline chloride has a lower activation energy (1.2 eV at lower temperatures below 40° and 2.0 eV at higher temperature between 40° and 73°, compared to 2.7 eV for the diethyl ether precipitated compound in the entire temperature range), shows electrical conductivity at room temperature that is several orders of magnitude higher than that crystallized from Et_2O, shows non-linear current-voltage characteristics, and displays polarization phenomena with relaxation times of more than an hour's duration. The electrical properties return to normal if the sample is heated to 100° and cooled. Thus, the effect of using petroleum ether for precipitating choline chloride appears to alter the latter's physical characteristics without really affecting the radiation sensitivity. It is possible that choline chloride precipitates out in a third crystal form from petroleum ether, trnasforms into β-form at temperatures at or above 100°, and then transforms back into α-form upon cooling to room temperature.

Although the conductivity data reported was very interesting, the equipment used was not adequate with respect to the features detailed below. Therefore, a new instrument was fabricated incorporating the following features. The design is similar to that reported by Kakado and Schneider[48] (and the details are shown in Figure 29).

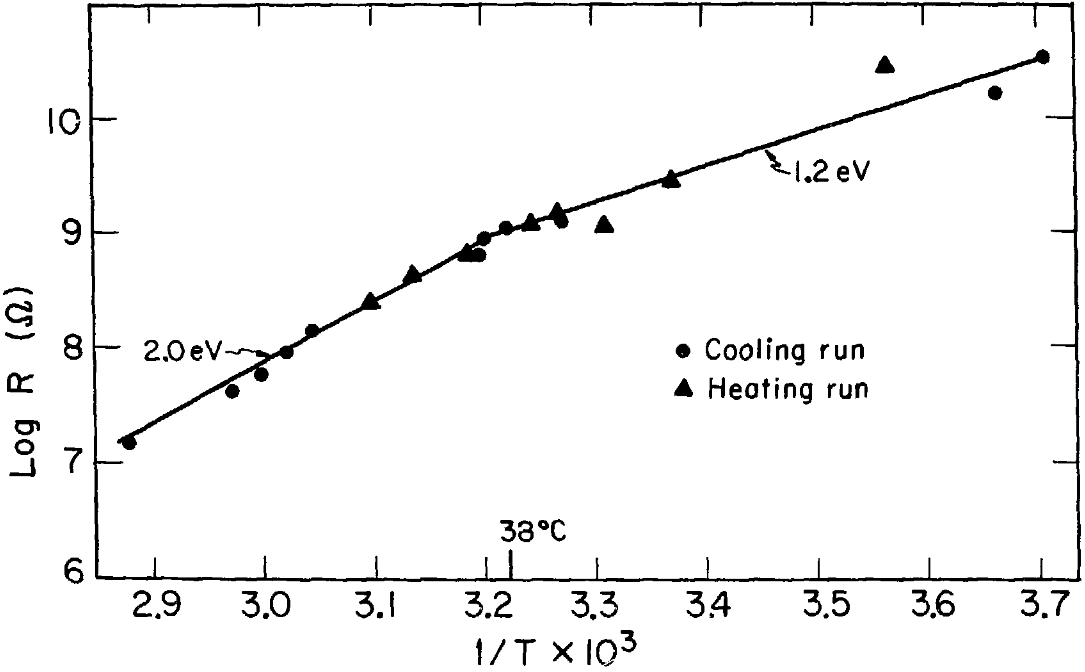

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Figure 28. Electrical conductivity of choline chloride precipitated from petroleum ether.

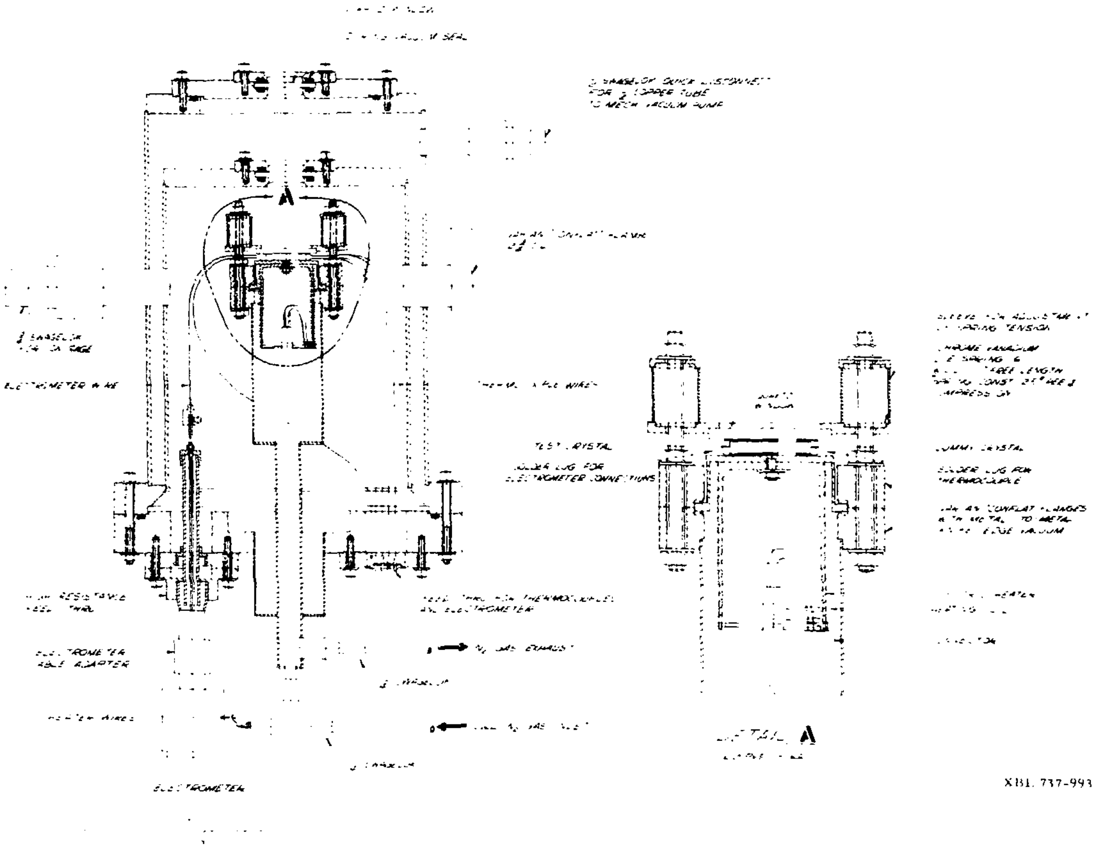

Figure 29. Improved apparatus for measuring electrical conductivity.

Fast and uniform rate of heating: The sample can be given a linear rate of temperature rise, ranging from 1°/min. to 60°/min. The electrical polarization effects, thus, can be studied at different pre-set temperatures. The conductivity behavior of irradiated choline chloride can also be studied before its radiolysis is complete, and from the data one can derive the population densities and the energy depths of the trapped electrons.

Wide temperature range: The conductivity can be measured at temperatures from -150° to +200°.

Photo conductivity: The samples can be illuminated, at any chosen wavelength, during the conductivity measurements through quatz windows.

Fast and high vacuum: The sample chamber can be evacuated very quickly to 10^{-6} torr pressure, and different gases can be introduced at known pressures. Thus, the effect of moisture and other ambients on conductivity can be studied.

Dummy Sample: A dummy sample is used to measure temperatures and to "sense" the temperature programmer, thus insuring a linear rate of heating. This will obviate any effect of electrical disturbances on the conductivity measurements.

Pressure and electrode effects: The sample can be sandwiched between different electrodes under pressure up to 2500 lb/sq. inch and its conductivity measured at any chosen pressure.

The sample to be studied, and the dummy sample, are sandwiched between two sets of metal sheet electrodes, and pressed by a set of six high-tension chrome-vanadium springs. The spring tension is independent of temperature and the pressure on the sample can be varied by compressing the springs to different lengths. The upper electrode is insulated from the chamber and from ground by a quartz disc, and is connected to a vibrating-reed electrometer through a high resistance and vacuum tight feed-thru. The lower electrode is electrically insulated from a copper disc by a thin mica sheet, which permits a thermal contact between the two. The copper disc is a face of a hollow cylinder, which is heated by a heater wound in the cavity. A stream of cold nitrogen passing through a solenoid valve strikes the bottom of the disc. The power to the heater and the solenoid is fed by a temperature controller. The controller consists of two units —— a power supply, made in our laboratory, to provide voltage for the heater and the solenoid and a programmer (Data-Trak Model-5300) to control the heating rate profile. The lower electrode is connected to a voltage source through a vacuum tight feed-thru. The set of electrodes sandwiching the dummy sample are welded to two (one at each crystal face) Chromel-Alumel thermocouple closed ends. The open ends f the thermocouple pass through fee-thru's and sense the temperature programmer to give a linear rate of temperature rise and record the temperature of the sample.

The sample is enclosed in a vacuum chamber by a double-walled stainless steel dewar. The dewar is equipped with quartz windows through which the sample can be illuminated to study photoconductivity. The vacuum chamber has large flange connections to a high speed oil diffusion pump, thus permitting rapid evacuation.

A vacuum valve in the system allows the chamber to be filled with different gases. It also may be connected to the fore pump without switching off the diffusion pump. Once the fore pressure is obtained, high vacuum is produced by opening the valve to the diffusion pump.

We have been able to reproduce the data reported above (Table VII) on the improved equipment. We also made some preliminary observations on the kinetics of the thermally stimulated currents in choline chloride.[48] The temperatures at which the trapped electrons are released, compouns, should show enhanced conductivity superimposed on the normal conductivity vs. temperature behavior. A pelleted choline chloride sample was γ-irradiated with a dose of 5 Mrads. The sample was then enclosed in the conductivity chamber and evacuated to 10^{-6} torr pressure and filled with dry helium to above 1 atmosphere. The sample was exposed to ambient moisture for about 10 min. during this process. The chamber is then isolated from the vacuum line. It is observed that the conductivity of the choline chloride sample decreased by a factor of 3 over a period of 24 hours at room temperature. After this it started increasing slowly with time. The chamber is pretty much air-tight and thus it can be safely assumed that the outside air leaked into the chamber only very slowly. Thus, the moisture absorption by the sample was basically the amount absorbed during the loading procedure. In addition, if there is leak, then the moisture absorption will only increase the conductivity as a function of time. It may be that the sample takes 24 hours to equilibrate with the absorbed moisture, but it is also possible that the decrease in conductivity during the first 24 hours is due to the decreased number of thermally detrapped electrons (the density of population of trapped electrons will decrease with time due to detrapping). The conductivity of the γ-irradiated choline chloride was 2-3 orders of mangitude higher than that of the unirradiated choline chloride. This could be partly due to the moisture absorption, but the decrease may be due only to the trapped electrons. This change seems very large when compared with the normal conductivity of the unirradiated choline chloride.

We did not pursue the studies, but the field of the thermally stimulated currents seems promising, especially if one could load the sample without exposure to ambient moisture.

B. Microwave conductivity measurements.

Due to inter-surface barriers in polycrystalline materials and possible electrode (charge carrier injection) effects in dc conductivity measurements, the results are questionable. Therefore we decided to do electrodless conductivity measurements at microwave frequencies (≈10 GHz). At these frequencies inter-surface barriers do not play any significant role. The general procedure and detailed theory of this method has been discussed in the literature.[49,50] We can also measure the sign and mobility of charge carrier independently using this method.

A bimodal cavity resonating at 9.5 GHz is used for the measurement of charge carrier concentration, their signs, and their mobilities. The detailed apparatus has been described by Bogomolni.[51] We used choline chloride in the form of a pellet compressed to 10,000 Kg/cm^2 of about 3 mm diameter and 0.5 mm thickness. The pellet is then sealed between very thin films of polyethylene and loaded in the cavity. All operations are done in a dry box to avoid excessive absorption of moisture. Further, the sample is heated in the cavity by the flow of preheated nitrogen. The temperature is measured by a copper-constantan thermocouple by placing it in the path of outgoing nitrogen. The results of the experiments are reported below.

We found a sharp increase in conductivity at the transition temperature at microwave frequencies too. The estimated increase is at least two orders of magnitude. The changes are reversible during heating and cooling of the sample. We could not exclude moisture in these measurements as much as we could in dc measurements. Moisture does increase dc conductivity of the α-form significantly while not having much effect for the highly conducting β-form. This may explain the smaller increase in the conductivity from the α-form to the β-form in the present method. Futhermore, conductivities tend to be larger in ac measurements due to the absence of effects of inter-surface barriers in polycrystalline materials.

The mobility and sign of charge carriers can be estimated by the following equations:

$$\frac{\Delta Q}{Q} = K_1 \sigma \frac{V_s}{V_c} \tag{1}$$

$$\Delta P = K_2 \frac{\Delta Q}{Q} \mu H \tag{2}$$

where ΔQ is the difference in Q between the loaded and empty cavity σ is conductivity, V_s and V_c are volumes of sample and cavity, ΔP is the change in power upon the application of magnetic field H, and

μ is the mobility of charge carriers. Q, the "quality factor of a resonator", is associated with microwave power losses due to the conductivity of the metal walls of the cavity and the backing material.

As one can see from the equations, for low conducting materials, ΔP, the experimentally measured quantity, will be very small unless the sample size is large. The sample size cannot be increased indefinitely due to difficulties arising by virtue of a large decrease in Q, and thus in the tuning of the cavity. Also, the assumptions used to derive (1) and (2), such as non-distortion of fields in the cavity, will no longer be valid.

Choline chloride in the α-form has a very small conductivity and, therefore, a compromise was made for the size of the sample. It was found that the charge carriers in the α-form have at least an order of magnitude larger mobilities than the mobilities of charge carriers in the β-form. Furthermore, from the sign of ΔP, it was inferred that the α-form has negative charge carriers. The mobility values in the α-form varied between -0.3 to -1.0 cm^2/volt-sec. The mobility μ is given by

$$\mu = \frac{e\tau}{m^*} \tag{3}$$

where τ is the relaxation time, m^* the effective mass of carriers of charge e. The low mobility of charge carriers in the β-form may be due to the larger effective mass. An estimate of the mobility of protons in the β-form of the choline chloride is about 10^{-8} cm^2/volt-sec (private discussion with Prof. A. M. Portis). The estimation is obtained as follows: The velocity of protons, v, at 350°K is $\approx (3\ k_B T/m)^{1/2} = 3 \times 10^5$ cm/sec. If the mean free path, ℓ, is assumed to be 5 Å, then the relaxation time,

$$\tau = \frac{\ell}{v} = \frac{5 \times 10^{-8}}{3 \times 10^{5}} = 1.6 \times 10^{-13} \text{ sec. Therefore,}$$

$$\mu = \frac{e\tau}{m} = \frac{1.6 \times 10^{-19} \times 1.6 \times 10^{-13}}{1.66 \times 10^{-24}} \approx 10^{-8} \text{cm}^2/\text{volt-sec.}$$

If this is so, the proposed protonic charge carriers fits the data well.

C. Infrared absorption studies.

The infrared spectra were determined as follows: One mg of the crystals is mixed thoroughly with 100 mg of KBr, and the mixture is ground with a mortar and pestle for 10 min. in a glove box; the latter is filled with very dry N_2 to avoid absorption of atmospheric moisture by the deliquescent choline chloride crystals. The solid mixture is then further dried on a vacuum line (10^{-4} torr at 100° for 2 hours). The dried samples are sandwiched between KBr powder in a metal die (The Barnes Engineering Company) and pressed into a pellet, and the pellet is kept in the die for the IR measurements. The die is wrapped with a heating tape connected to a variable voltage source, and a Chromel-Alumel thermocouple is attached to the die for temperature measurements. The spectra are recorded on a Perkin-Elmer Model-137 infrared spectrometer. The deuterated cholines were synthesized as described in a previous publication.[3] The preparation of other analogs has been reported earlier.[4]

One would expect that the intermolecular interactions in the two polymorphs (α- and β-forms) would be different. These differences might be responsible for the extreme differences in radiation sensitivity of the two polymorphs of choline chloride. Polymorphs are known to exhibit different optical absorption spectra in the far infrared region (2.5-15 μ).[52,53]

Figures 30 through 36, a and b, show the infrared spectra of the choline analogs in the α- and β-forms, respectively (the different forms are indicated by their conductivity behavior). As reported earlier, the density changes upon phase transformation and therefore the transparent pellets become transluscent upon phase transformation, and scatter more lignt. Thus, spectra were also recorded after repressing the pellet following phase transformation. This improves the spectrum without changing its features. There is no change caused in spectrum of any compound in a given crystal form by a change in the temperature. Thus, the spectrum taken at a temperature just below the phase transition temperature is almost identical to the one taken at room temperature. The changes that do occur are due only to phase transitions. These changes are reversible; that is, when a spectrum changes on going from an α- to a β-form, the α-form's spectrum reappears when the sample is cooled below the α-β transition temperature. The infrared absorption takes place due to the excitation of vibrational modes of the atoms in a molecule. These modes could be either stretching or bending modes. The frequency, ν, of these modes is given by

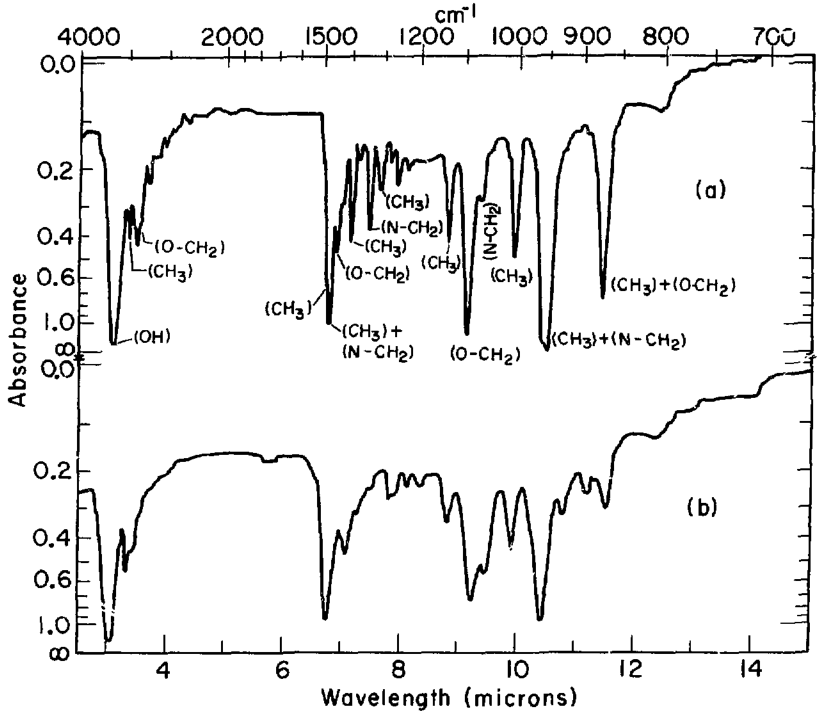

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Figure 30. Infrared absorption of choline chloride. (a) α-form at room temperature. (b) β-form at approx. 100°.

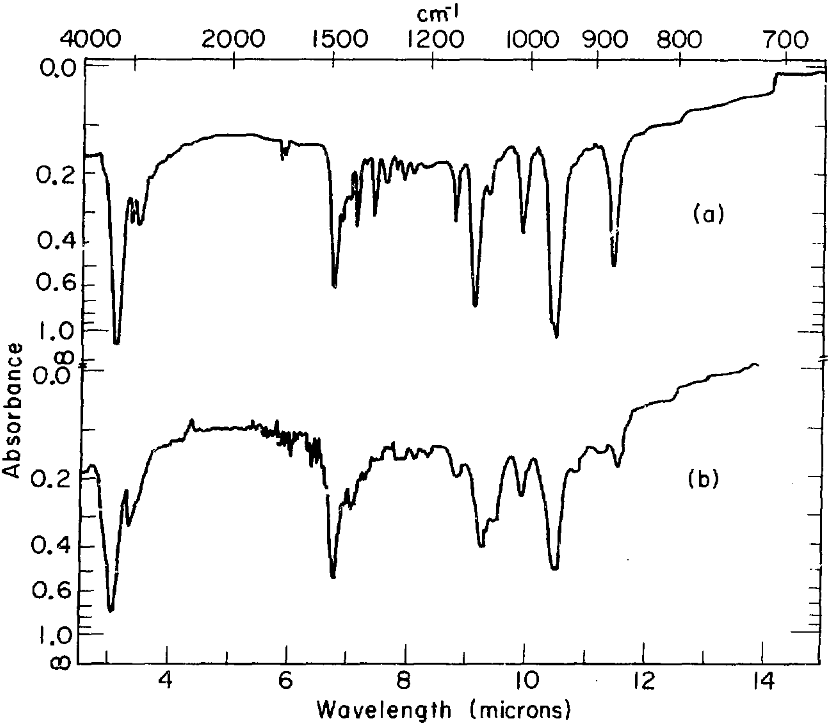

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Figure 31. Infrared absorption of choline bromide. (a) α-form at room temperature. (b) β-form at approx. 120°.

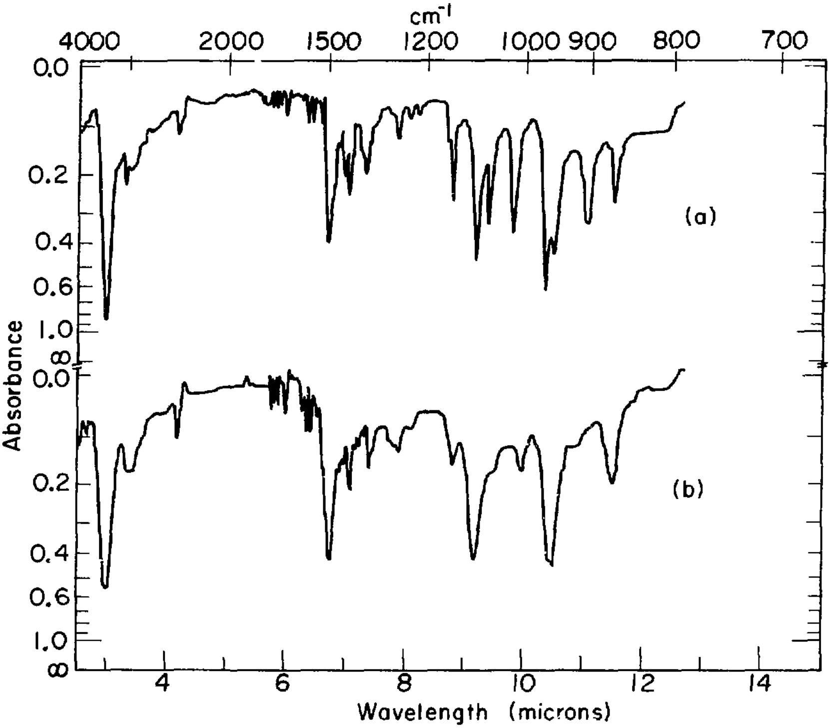

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Figure 32. Infrared absorption of choline iodide. (a) α-form at room temperature. (b) β-form at approx. 125°.

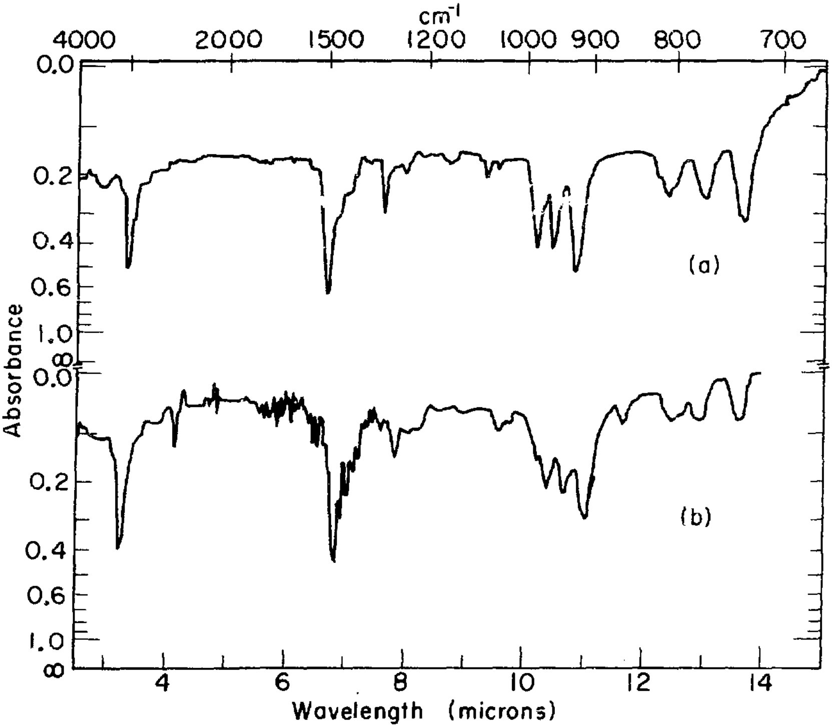

Figure 33. Infrared absorption of the chloro analog, $[(CH_3)_3NCH_2CH_2Cl]^+Cl^-$. (a) α-form at room temperature. (b) β-form at approx. 175°.

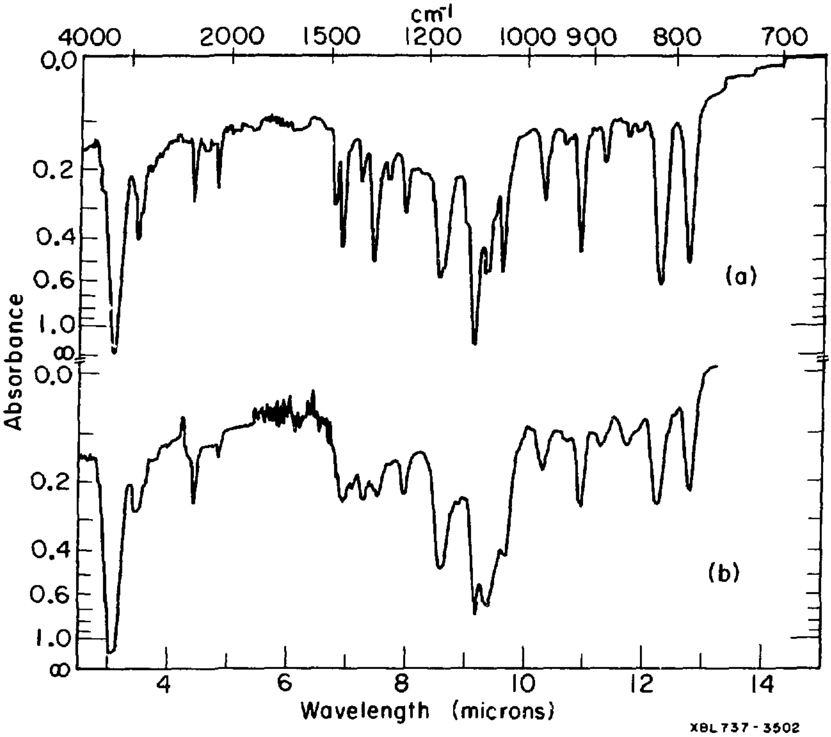

Figure 34. Infrared absorption of the methyl deuterated analog, $[(CD_3)_3NCH_2CH_2OH]^+Cl^-$. (a) α-form at room temperature. (b) β-form at approx. 100°.

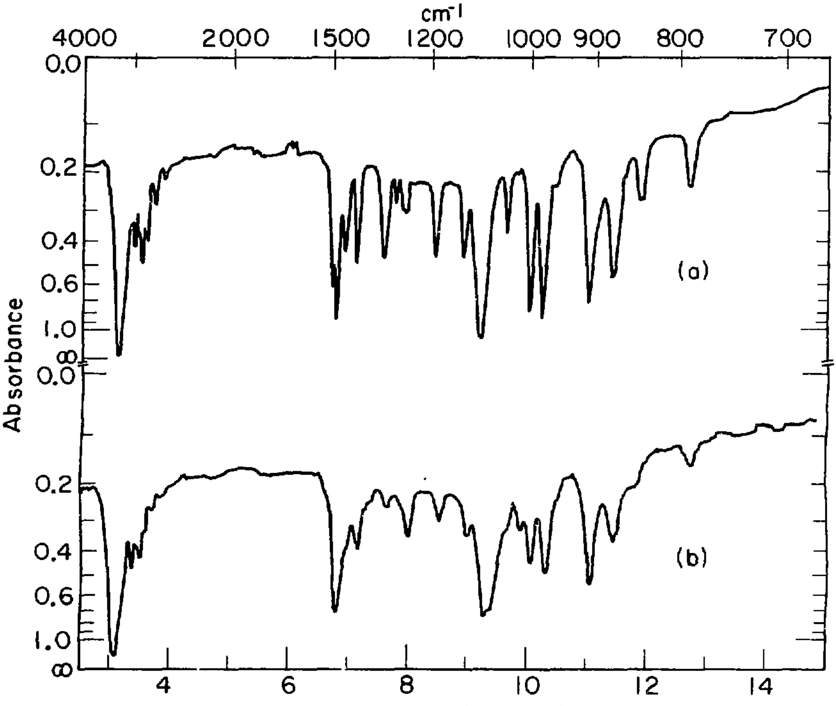

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Figure 35. Infrared absorption of N-methylene deuterated analog, $[(CH_3)_3NCD_2CH_2OH]^+Cl^-$. (a) α-form at room temperature. (b) β-form at approx. 100°.

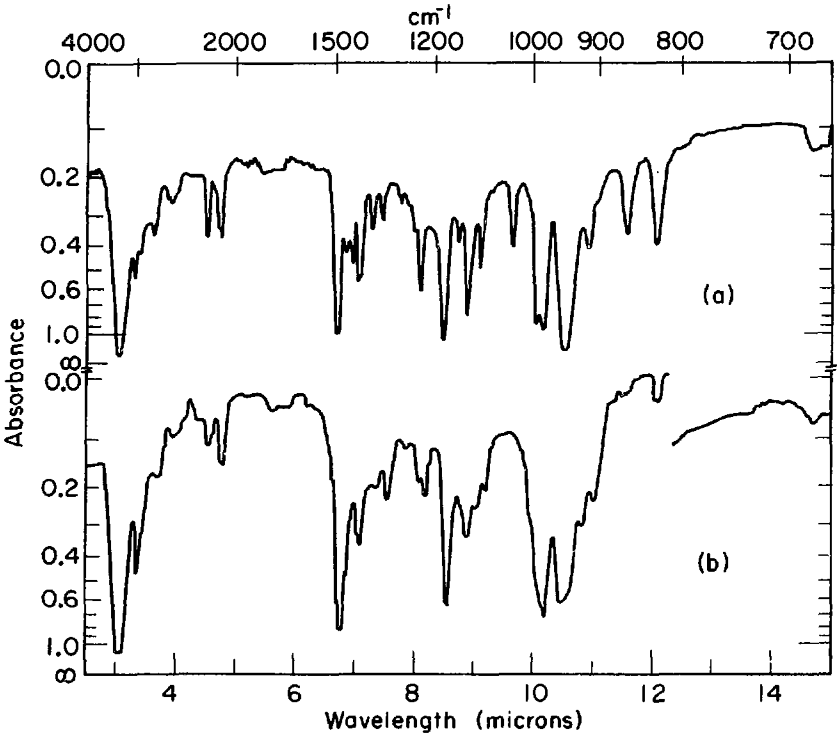

Figure 36. Infrared absorption of O-methylene deuterated analog, $[(CH_3)_3NCH_2CD_2OH]^+Cl^-$. (a) α-form at room temperature. (b) β-form at approx. 100°.

$$\nu = \sqrt{2\pi \frac{f}{m_{eff}}}$$

where f is the force constant of the bond and m_{eff} is the effective mass of the bound atoms.

When heavier atoms like C, N, O are bonded to H, the effective mass is 1. The force constants depend on the type of bond and its strength. Thus, the bonds in different types of atoms and different kinds of vibrational modes absorb at different frequencies. Further, if we substitute the H-atoms with deuterium, the frequencies are decreased by a factor of $1/\sqrt{2}$ due to the increase of the effective mass to 2. Therefore, deuterium substitution can be used to assign absorption peaks due to different types of bonds. The decrease in frequency by $1/\sqrt{2}$ is correct for C-H stretching modes, but for bending modes the effect is complicated due to the interaction of modes arising from different types of vibrations. This usually occurs when the frequencies of these are close to each other. Thus, the bending modes in the C-H bond have frequencies close to the stretching modes of C-C, C-O, and N-C bonds and, therefore, the shift of frequencies is not well defined. However, the disappearance of a peak upon deuteration can be used to assign different frequencies to different modes and bonds. The method of successive deuteration and comparison of respective spectra is used to give a tentative assignment as shown in Figure 30. For example, $[(CD_3)_3NCH_2CH_2OH]^+Cl^-$ shows no (or greatly diminished) peaks at 3.35, 6.7, 7.1, 7.6, or 9.9 μ; consequently, these peaks have been assigned to methyl C-H bending and stretching modes. $[(CH_3)_3NCD_2CH_2OH]^+Cl^-$ shows no peaks at 7.4, 9.4, or 10.5 μ, and a much diminished peak (compared to the undeuterated compound) at 6.8 μ. $[(CH_3)_3NCH_2CD_2OH]^+Cl^-$ shows no (or greatly diminished) peaks at 3.5, 6.9, 9.1, or 11.4 μ.

The principal differences between the infrared spectra of the α- and β-forms of choline chloride appear to be in these $O\text{-}CH_2$ peaks. They are prominent in the α-form, and are lacking, or greatly reduced, in the β-form. The vibrational differences thus indicated may be related to the fact that the α-form of $[(CH_3)_3NCH_2CD_2OH]^+Cl^-$ is less than half as radiation sensitive as the α-form of ordinary (fully protonated) choline chloride.[25] Selective deuteration in any of the other three positions (methyl, N-methylene, or hydroxyl) leaves the radiation sensitivity essentially unchanged, i.e., within 10% of the value of the ordinary compound. It appears that a movement of hydrogen atom out of the $O\text{-}CH_2$ group is a key process in the radiolysis —— and both intramolecular and some intermolecular transfers of these hydrogens have been shown by previous studies.[9]

The O-H bond stretching frequencies for hydrogen-bonded systems are shifted towards longer wavelengths; the normal absorption for free O-H groups is 2.74-2.79 μ.[54] The stretching frequency for the choline compounds (all of those studied here) comes at 3.0-3.1 μ, a substantiation of the hydrogen bonding that X-ray crystallography has already indicated as being present in choline chloride. Choline iodide seems to have less hydrogen bonding (the OH peak seems to have less hydrogen bonding (the OH peak is at 3.0 μ compared to 3.1 μ for the rest of them).

The differences between the α- and β-forms of the other analogs are also obvious. The bands in the β-form seem to be broadened, probably due to molecular rotational absorptions superimposed upon the normal vibrational modes. The α- and β-forms of the bromide have IR spectra that are virtually identical with those of the chloride, an interesting observation since the bromide is the only choline analog that shows any of the chloride's amazing radiation sensitivity. On the other hand, the spectra of the iodide and of the chloro analog, which show no anomalous radiation sensitivity, are considerably different from those of the chloride and bromide.

The temperature at which the changes in the spectra occur agree with the temperature at which the conductivity changes sharply.

We have also examined the infrared spectra of ordinary choline chloride (α-form) and of the γ-irradiated (5 Mrads) compound. There were no detectable differences in these spectra, indicating that no absorption bands, in 2.5-15 μ range, are created in choline chloride upon irradiation (at least they are not present at room temperature).

CHAPTER VI

EFFECTS OF H-ATOM EXPOSURE AND VACUUM ULTRAVIOLET IRRADIATION ON THE RADIOLYSIS OF CHOLINE CHLORIDE

It has been reported in the literature[55, 56] that the ESR spectra resulting from H-atom irradiations of organic compounds are simpler than those resulting from more conventional, ionizing radiation, such as γ-rays, X-rays, or electron beams. The reason for this appears to be that the dominant mechanism is a simple hydrogen abstraction, giving a radical and hydrogen gas: $RH + H\cdot \rightarrow R\cdot + H_2$. Ackerman and Lemmon have reported that hydrogen gas is produced in significant amounts upon the radiolysis of choline chloride.[11] Lemmon and Nath have investigated the effect of hydrogen atom exposure of choline chloride and found that radicals so produced had characteristics similar to the ethanol radical that appears upon γ-irradiations.[57] A possible mechanism for the production of ethanol radicals was also suggested. It seemed, therefore, of potential value in understanding choline chloride's radiolysis mechanism to extend these studies and to determine whether the H-atom exposures also initiate the same highly efficient radiolysis as does the ionizing radiation.

It has also been reported earlier that unirradiated choline chloride does not have any optical absorption above 200 nm and, therefore, it does not undergo any decomposition upon irradiation with light of wavelength above 200 nm. The production of H-atoms is accompanied by production of light in the vacuum ultraviolet range (emission spectrum of H_2) and, therefore, we also studied the effects of irradiation with light below 200 nm (where choline chloride absorbs).

The apparatus used to expose choline chloride to atomic hydrogen is shown in Figure 37. This is a slight modification of the apparatus used by Lemmon and Nath. We have used a more powerful microwave

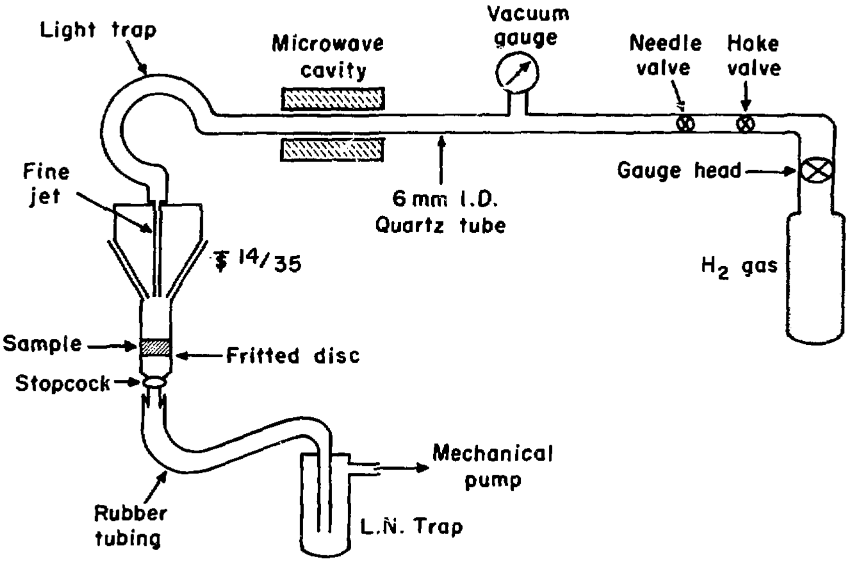

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Figure 37. Apparatus used to expose choline chloride to H-atoms.

generator (2450 MHz and 1000 watt) supplied by a Litton Industries Model L-3189 magnetron. In addition, a light trap is also used to isolate the effect of H-atoms from that of ultraviolet light. The UV light does not reach the choline chloride due to multiple reflections by the trap. The fine jet is provided to impart some speed to the flow of hydrogen atoms. In a glove box the choline chloride crystals were placed on the glass frit and then protected by a stopper from atmospheric moisture. This assembly was then attached to the quartz tube passing through the cavity. After the assembly was evacuated, H_2 was passed into the system, and its pressure maintained at 100-250 microns, by continuously operating the mechanical pump, and by suitably adjusting the needle valve. The microwave generator was operated at about 1000 watts for 8 hours. Although we have made no direct determinations of the hydrogen atom fluxes obtained in the apparatus, we monitored its performance by occasionally substituting malonic acid for the choline chloride. This gave us the 2-line ESR spectrum, reported by Cole and Heller,[55] and interpretable as $\cdot CH(CO_2H)_2$. We found that the spectrum is stronger if we maintain the pressure between 100-250 microns compared to higher pressure. The samples were cooled (for some experiments) by directing a jet of cold nitrogen at the outside of the tube. Since the H-atoms do not have sufficient penetrating power, the powder sample was tapped occasionally so that most of the sample was, at one time or another, exposed to the atomic hydrogen. The apparatus used for vacuum UV studies is shown in Figure 38. It is similar to the one used for H-atom exposures except that the light trap is replaced with a straignt tube and

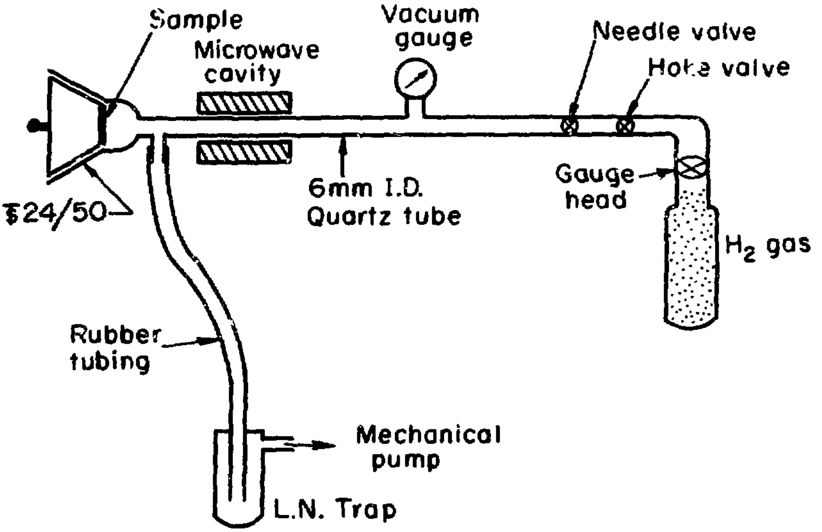

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Figure 38. Apparatus used to expose choline chloride to vacuum ultraviolet.

the choline chloride (pelleted) is mounted vertically on a glass stopper. The evacuation is done from the side tube. In this way the choline "looked" directly down the tube that passed through the cavity, getting full irradiation by the UV. The hydrogen atoms were pumped through the side arm.

We tried to produce ethanol radicals with this improved H-atom exposure apparatus. We could not get any ESR signal from the irradiated sample, even at the highest gain in the Varian Model E-3 spectrometer. We also varied the temperature of the sample during exposure, to take into account radical decay, but still failed to detect an ESR signal. However, malonic acid gave strong signal under identical conditions, suggesting H-atoms are indeed formed in the apparatus. We suspected that the original observations were due to the UV irradiation, since the light trap was not used at that time. We have now confirmed, using the UV irradiation apparatus, that the signal obtained was indeed due to the UV. We irradiated a choline chloride pellet at room temperature for 3 hours. The pellet was then broken into small pieces and inserted into a quartz tube in a glove box. The ESR signal of the irradiated sample is shown in Figure 39. The intensity of the signal is small, but its characteristics are very similar to those of the ethanol radical that is produced upon γ-irradiation. We can perhaps assume that, due to constant pumping, only a very small fraction of H-atoms, if any at all, could be striking the sample. Malonic acid in the same position does not give the stable, 2-line spectrum that is obtained with H-atom exposure.

Since vacuum UV irradiation produces ethanol radicals, the

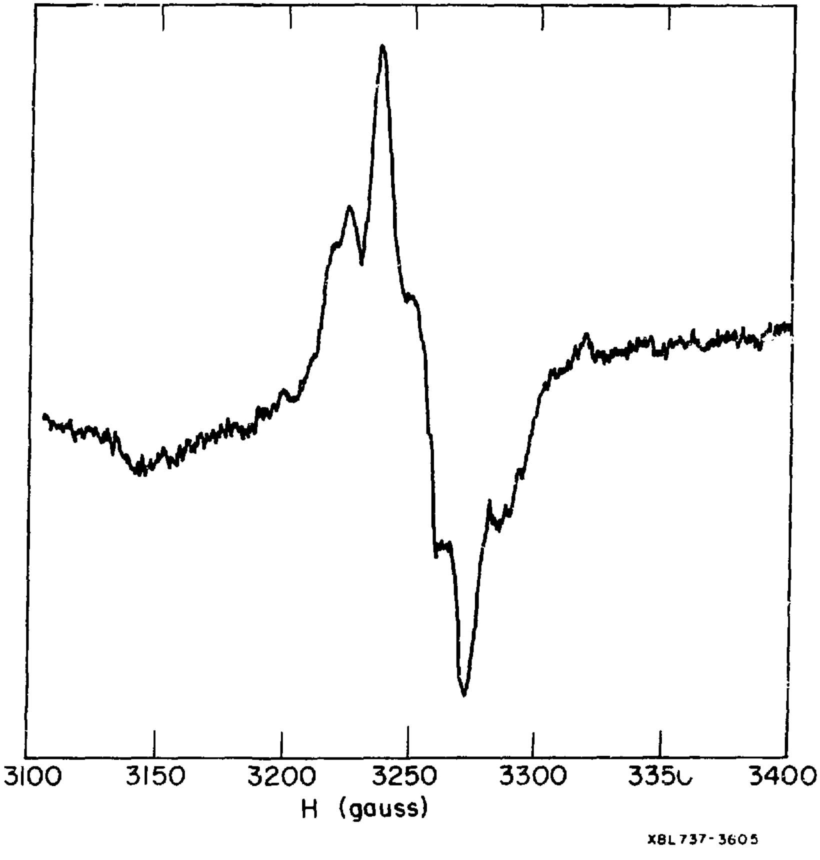


Figure 39. ESR spectrum of vacuum ultraviolet exposed choline chloride.

question arises whether the mechanism of this photolysis, if it occurs, is similar to that of radiolysis. The UV photon intensity is not comparable to the γ-flux, nor is the penetration of UV photons, and therefore the concentration of radicals formed during photolysis is about three orders of magnitude less than that formed by, say, 3 Mrad dose of γ-irradiation. To study the photolysis we irradiated samples of labeled choline chloride with vacuum UV for 3 hours; the sample was maintained below 0° during irradiation (by the jet of cold nitrogen). The irradiated samples were then heated for 2 hours at 50° and analyzed for decomposition. We found TMA as the only radioactive decomposition product and quantitatively the photolysis was 0.45 percent. An unirradiated sample (control) heated fro 2 hours at 50° shows only 0.15 percent decomposition. These results indicate that the photolysis mechanism is identical to the radiolysis mechanism and the energy exchange processes in choline chloride are independent of the photon energy (crystallography is also complicated due to choline chloride's radiolysis during its exposition to X-rays).

Labeled choline chloride (no γ-irradiation) was also subjected to atomic hydrogen exposure at room temperature for 8 hours. The exposed samples (and controls with no H-atom exposure) were analyzed without any post-irradiation thermal treatment. We found as much as 9.3 percent decomposition for the irradiated samples (0.6 percent for the control). The decomposition depends very much on the way the sample is distributed on the glass frit —— the amount of decomposition being dependent on the surface area exposed. Since the H-atoms cannot penetrate the crystals, this is a remarkably high decomposition, and it indicates an important role for these atoms in the radiolysis mechanism. An unexpected feature of this decomposition is that, unlike what is observed in γ-irradiations, much polymer (5.5 percent; TMA 3.8 percent) is formed as a product. We feel that H-atoms are the actual chain propagating species in the radiolysis of choline chloride. The polymer formation is probably due to the extensive H-atom exposure of the product TMA and choline chloride at the surface. Their role will be suggested in the mechanism to be presented in the next chapter.

We subjected γ-irradiated labeled choline chloride to the H-atom exposure at room temperature for two hours. A control was kept at room temperature with no H-atom exposure. There was no difference in the radiolysis values for the two. It seems that H-atoms are not increasing the radiolysis due to their decay by interaction with ethanol radicals in preference to their causing chain radiolysis. The decay could be visualized as follows:

$$(a)\quad \cdot CH_2CH_2OH + H\cdot \longrightarrow CH_3CH_2OH$$

$$(b)\quad \cdot CH_2CH_2OH + H\cdot \longrightarrow CH_3CHO + H_2$$

CHAPTER VII

PROPOSED RADIOLYSIS MECHANISM AND FUTURE INVESTIGATIONS

The following mechanism appears to account for all our observations, especially specific involvement of ethanol radicals, electrons, and hydrogen atoms, on the radiation decomposition of crystalline choline chloride:

(1a) $(CH_3)_3\overset{+}{N}CH_2CH_2OH \rightsquigarrow (CH_3)_3\overset{+}{N} \cdot\cdot\ CH_2CH_2OH$

(1b) $(CH_3)_3\overset{+}{N}CH_2CH_2OH \rightsquigarrow \underset{\text{(hole)}}{(CH_3)_3\overset{+}{N}CH_2CH_2\overset{+}{O}H} + e^-_{trap}$

(2) $(CH_3)_3\overset{+}{N} \cdot\cdot\ CH_2CH_2OH \longrightarrow (CH_3)_3\overset{+}{N}\cdot + H_2C\dot{-}CH_2OH$

(3a) $e^-_{trap} \longrightarrow e^-_{free}$

(3b) $H_2C\dot{-}CH_2OH + e^-_{free} \longrightarrow [:CH_2CH_2OH^*]^-$

(4) $[:CH_2CH_2OH^*]^- + (CH_3)_3\overset{+}{N}CH_2CH_2\overset{+}{O}H \longrightarrow$

$(CH_3)_3\overset{+}{N}CH_2CH_2OH + CH_3CHO + H^{\cdot}$

(5) $H\cdot + (CH_3)_3\overset{+}{N}CH_2CH_2OH \longrightarrow (CH_3)_3\overset{+}{N}H + CH_3CHO + H\cdot$

(6) $(CH_3)_3\overset{+}{N}\cdot + H\cdot \longrightarrow (CH_3)_3\overset{+}{N}H$

Overall reaction

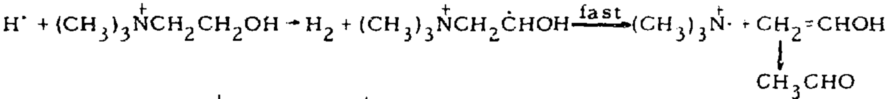
$$2\ (CH_3)_3\overset{+}{N}CH_2CH_2OH \longrightarrow 2\ (CH_3)_3\overset{+}{N}H + 2\ CH_3CHO$$

For simplicity, the chloride ion has been omitted from these reactions, although it might be important for the stabilization of the "holes" in (1b) and (4).

Reactions (1a) and (1b) account for the appearance, upon γ-irradiation of choline chloride at -196°, of biradicals (ESR spectrum at 1600 G), and trapped electrons (thermoluminescence and optical absorption studies). When electrons, released due to the ionization of molecules, get trapped into metastable energy states, the molecules are left with excess positive charge and are called holes. However, we have not seen any ESR spectrum corresponding to these holes or electrons. A small signal might have been masked by a broad and large signal due to the biradicals and the ethanol radicals at 3200 G. It may also be that spin-lattice relaxation times are too short to permit us to see the signal.

Reaction (2) accounts for the decay of the biradical upon heating the irradiated sample, due to the diffusing apart of the two monoradicals, and eventually giving the ESR signal interpretable as that of ethanol radicals. However, we have not seen any ESR signal corresponding to the trimethyl amine radicals. We feel that this is due to rapid spin-lattice relaxation in choline chloride matrix. We irradiated choline chloride at room temperature and above, thereby irradiating the trimethylamine hydrochloride formed by radiolysis and found no signal from trimethylamine radicals. Symon has reported,[13] and we have confirmed, that by γ-irradiation of trimethylamine hydrochloride an ESR signal is obtained interpretable as that of trimethylamine radicals. It is, of course, possible that the product might have been in the form of free base, rather than the hydrochloride salt, in which case no trimethylamine radical will be formed upon irradiation.[13] But then we have to postulate that the free base, a gas at ambient temperature, is trapped in the choline matrix such that it does not escape even by evacuation at 70°. This seems unlikely.

Reactions (3a) and (3b) are postulated for the detrapping of electrons and their subsequent reaction with the ethanol radicals to give the excited anionic specie. We have found that (1) the radiolysis can be induced at low temperature by transferring electrons from photodonors; (2) the radical decay is enhanced in the presence of photodonated electrons; (3) the radiolysis is retarded by the electron-accepting ambients; (4) the radiolysis is also retarded by doping the crystals with KI; (5) heating at 150° before irradiation leads to diminished radiolysis; (6) large, slowly grown crystals are more resistant to radiolysis than are microcrystallites; (7) the extent of decomposition is increased for a given radiation dose, if the dose delivery is interrupted by periods of heating at 50°; (8) the radical decay is faster than the radiolysis; (9) the radiolysis can be enhanced by exposure to thermal electrons. These observations are interpreted as reflecting a prominent role for detrapped electrons in the radiolysis mechanism. It has also been found that choline chloride and choline bromide are the only analogs that give ethanol radical upon irradiation. This coupled with the fact that these are the only compounds which are abnormally radiation sensitive suggest that ethanol radicals are necessary for the chain mechanism. This is further confirmed by photoreduction of ethanol radicals at temperatures where chain does not propagate and its subsequent diminished radiolysis. In view of these observations, it seems very reasonable that the electrons and the ethanol radicals are necessary for the radiolysis, and any mechanism proposed should include both of them. We do not have any evidence for the existence of the excited anionic specie and its subsequent fate. Reaction (4) is simply postulated to account for the fact that H_2 is found as a minor product in choline chloride's decomposition,[11] and that hydrogen-atom exposure produces large decomposition in choline chloride. A possible pathway for the decomposition of unirradiated choline chloride by hydrogen atoms can be, via hydrogen atom abstraction, as follows:



$$H^{\cdot} + (CH_3)_3\overset{+}{N}CH_2CH_2OH \rightarrow H_2 + (CH_3)_3\overset{+}{N}CH_2\dot{C}HOH \xrightarrow{fast} (CH_3)_3\overset{+}{N}\cdot + \begin{array}{c} CH_2{=}CHOH \\ \downarrow \\ CH_3CHO \end{array}$$

$$H\cdot + (CH_3)_3\overset{+}{N}\cdot \longrightarrow (CH_3)_3\overset{+}{N}H$$

But, to account for the decomposition of γ-irradiated choline chloride, a chain mechanism must be proposed, since there are definitely no indications of large concentrations of hydrogen atoms in the ESR spectrum of γ-irradiated choline chloride and the concentration of the ethanol radicals themselves is less than 0.1 percent. We are unable to provide any more specific pathway for reaction (5) because of insufficient data, but the driving force for this reaction may be an attack by hydrogen atoms at the nitrogen (the N-H and N-C covalent bond energies are approximately 84 and 49 Kcal/mole). However, we have proposed reaction (5) on circumstantial evidence only. Reaction (6) accounts for the chain termination.

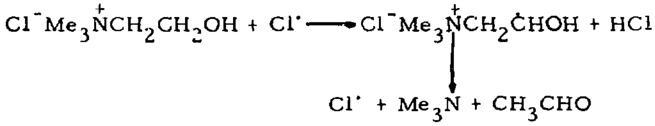
The reason as to why this chain is carried only in choline chloride and choline bromide seems to be that these are the only analogs that give the ethanol radicals when subjected to ionizing radiation. The other radicals probably do interact with detrapped electrons, for which we have found evidence in preliminary thermoluminescence studies, to give the excited species. But these species do not produce H-atoms. If this is the case, then other choline salts should be equally susceptible to attack by H-atoms, even though they are less susceptible to chain decomposition by ionizing radiation. Thus, H-atom irradiations of choline analogs should be investigated.

It is also possible that the crystal structure of other analogs may be such that the chain propagation is prohibited, although H-atoms are available to dissociate the choline molecule. It has already been reported that choline chloride and choline bromide exist in orthorhombic form at room temperature while choline iodide exists in monoclinic form.[7] Therefore X-ray crystallographic studies of other analogs in the low and high temperature forms should be investigated.

We have proposed that the β-form of choline chloride is radiation insensitive because of its protonic conductivity. No direct evidence has been provided, and therefore experiments to investigate the charge carriers in the β-form will be useful. Of course, again, the crystal structure may prohibit the radiolysis chains. Infrared studies of choline chloride and its analogs on an improved (better resolution) equipment together with solid state nuclear magnetic resonance studies will be complementary to the crystallography in the structure determinations.

Professor W. H. Hamill has proposed that the chain reaction may be propagated by chlorine atoms.[58] He suggested that choline atoms arise by virtue of ionization of chloride ions.

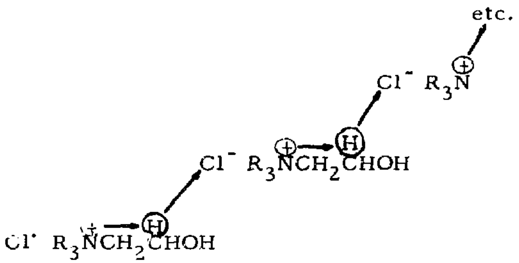
$$Cl^- \longrightarrow Cl^\cdot + e^-_{trap}$$



$$\begin{array}{l} Cl^-Me_3\overset{+}{N}CH_2CH_2OH + Cl^\cdot \longrightarrow Cl^-Me_3\overset{+}{N}CH_2\dot{C}HOH + HCl \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad Cl^\cdot + Me_3N + CH_3CHO \end{array}$$

This mechanism would suggest that we should find Cl_2 (obtained by recombination of Cl-atoms) in the radiolysis products. Ackerman and Lemmon sought for detectable amounts of Cl_2, but were unsuccessful.[11] It does not provide for the fate of the trapped electrons and the observations we have reported with regard to the involvement of electrons and ethanol radicals. However, this proposed mechanism can be tested by bombarding labeled choline chloride with chlorine atoms and looking for decomposition.

Dr. A. O. Allen argues that if we suppose that the chlorine atom exists in a free state and able to move around, this formulation would not explain the dependence of the yield on the crystal structure.[59] According to Dr. Allen, the radiation removes an electron from the chloride ion and it is trapped somewhere, producing a "hole" or condition of excess positive charge in the neighborhood of a chlorine atom. This would have the effect of displacing the positive charge from the neighboring nitrogen in the direction of the ethanol group and hence facilitate the departure of a proton from this group towards the chloride ion of an appropriately placed neighboring molecule, thereby forming a hydrogen chloride molecule. This in turn would cause the displacement of charge from the nitrogen of this neighboring molecule, as shown schematically below, and induce displacement of another proton forming another molecule of HCl and so on. With each such displacement a molecule of trimethylamine and of CH_2=CHOH (enol form of acetaldehyde) would form. The process could be represented as follows:



On this hypothesis, the chains would seem to be initiated by holes rather than electrons. Dr. Allen's hypothesis assumes that an αH of the ethanol group in choline chloride is located near a Cl⁻. His calculations based on published crystallographic data[7] show that Cl⁻ is 3.15 Å from the nearest αH. This proposal could be tested by injecting "holes" in choline chloride (unirradiated) and deterimine the effect of hole injection on the radiolysis, although the reduction of radiolysis in electron accepting ambients and increase in case of photodonation of electrons will still have to be explained.

Symons has also proposed a chain mechanism which is initiated by a hole, <u>viz.</u>, Cl· atom, but propagated by $Me_3\overset{+}{N}\cdot$ radicals.[13] According to him, the Cl· is trapped during γ-irradiation of choline chloride at liquid nitrogen temperature (-196°)

$$Cl^{\cdot} + Cl^{-} \longrightarrow Cl_2^{-} .$$

During thermal treatment, the chlorine attacks a neighboring choline cation and the sequence follows:

$$Cl^{\cdot} + Me_3\overset{+}{N}CH_2CH_2OH \longrightarrow HCl + Me_3\overset{+}{N}CH_2\dot{C}HOH$$

$$Me_3\overset{+}{N}CH_2CHOH \xrightarrow{slow} Me_3\overset{+}{N}\cdot + CH_2{=}CHOH$$

$$Me_3\overset{+}{N}\cdot + Me_3\overset{+}{N}CH_2CH_2OH \longrightarrow Me_3\overset{+}{N}H + Me_3\overset{+}{N}\ CH_2\dot{C}HOH$$

The radical $Me_3\overset{+}{N}CH_2\dot{C}HOH$ has not been observed by anyone. This model also suggests that one should find Cl_2 in the products. If $Cl^{\cdot}$ are responsible for the radiolysis, then it is hard to understand why the propyl analog, $[(CH_3)_3NCH_2CH_2CH_2OH]^{+}Cl^{-}$, and the ethyl analog, $[(C_2H_5)_3NCH_2CH_2OH]^{+}Cl^{-}$, are radiation resistant.

The possibility that trimethylamine radical, $(CH_3)_3\overset{+}{N}\cdot$, is the chain propagator has long been proposed in this laboratory also.[60] As a consequence, we were constantly aware of this during the present work. However, we are unable to construct any mechanism involving this radical as a chain propagator that also accounts for either (a) the role of free electrons or (b) the obvious connection between the ethanol radicals and the radiolysis. In addition, the interaction of electrons with trimethylamine radicals would result in trimethylamine, as compared to an excited anion (reaction 3b) in case of its interaction with the ethanol radicals; the latter are more likely to carry the chain decomposition.

In any case, it is hoped that the results discussed in this thesis and the proposed work will aid in understanding the unique solid-state phenomena that are occuring in irradiated crystalline choline chloride.

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