# The Role of Detrapped Electrons in the Radiolysis of Crystalline Choline Chloride[1]

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**Abstract:** Further investigations into the unique ionizing-radiation sensitivity of one crystalline form ($\alpha$) of choline chloride have shown that (1) the radiolysis can be induced at low temperature by phototransferring electrons from Brilliant Green and cadmium sulfide; (2) the radiolysis is retarded by the electron-accepting ambients $O_2$, $SF_6$, $N_2O$, and $I_2$; (3) the radiolysis is also retarded by doping the crystals with KI; (4) heating at 150° before radiolysis leads to diminished radiation decomposition; (5) illumination of the irradiated crystals by ultraviolet or visible light has no effect, whereas infrared light potentiates the 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 electrical conductivity of the $\alpha$ form appears to be electronic and ohmic, and that of the radiation-resistant form ($\beta$) appears to be protonic and nonohmic. In addition, esr studies have indicated that there is only one observable radical in the irradiated $\alpha$ form, and that there is a lack of correspondence between the kinetics of radical decay and that of radiolysis. These observations are interpreted as reflecting a prominent role for detrapped electrons in the radiolysis mechanism.

It has been known for many years that crystalline choline chloride, $[(CH_3)_3NCH_2CH_2OH]^+Cl^-$, is a remarkably radiation-sensitive compound.[2] It decomposes by a chain reaction that, under certain conditions of irradiation, gives $G_{(-M)}$ values as high as 55,000.[3] The anomalous radiation sensitivity is shown only by the crystalline form; in solution, the compound exhibits normal radiation stability.[4] The main radiolysis products, accounting for at least 95% of the final products, are trimethylamine and acetaldehyde.[5]

It has also been observed that the crystal's radiation damage can be deferred indefinitely by irradiating and storing at $-78°$.[3] Damage develops gradually over several hours at ambient temperature, and much faster at higher temperatures. However, at about 78° choline chloride undergoes a phase transformation (from orthorhombic to disordered cubic) and the higher temperature polymorph is a "normal," *i.e.*, radiation-resistant, one.[6,7] We refer to the orthorhombic, radiation-sensitive polymorph as the "$\alpha$ form" and the cubic, radiation-resistant crystals as the "$\beta$ form."

Since the radiolysis of the $\alpha$ form does not proceed at $-78°$, it appears that the thermal stimulation is required either for the diffusion of radicals (or other reactive species) or for the release of trapped electrons. It is known that a high concentration of radicals (partially identified as approximating the formula $\cdot CH_2CH_2OH \cdots Cl^-$)[3] are formed with a $G$ value of about 2 for the dosage we have used, *viz.*, approximately 3 Mrads. It is probable that electrons are trapped during irradiation, either on preexisting crystal defects or ones created during irradiation, and that the subsequent thermal release of these electrons enables them to react with the radicals, forming excited species that participate in self-propagating chains. In order to investigate a possible involvement of detrapped electrons in triggering a chain decomposition, we have observed the effects (on the $\alpha$ form's radiolysis) of prior thermal treatment, of added electron-accepting ambients, of photoelectron transfers, of photodetrapping of electrons, and of different crystal sizes. We have also compared the decay kinetics of the radicals with the kinetics of the radiolytic decomposition and investigated the dc electrical conductivity of both the $\alpha$ and $\beta$ forms. Finally, we report some interesting observations on repeated cycles of irradiating and heating the $\alpha$ form.

## Experimental Section

**Choline Chloride.** For the experiments described here we used crystalline choline chloride (Eastman Organic Chemicals) and the methyl-$^{14}C$-labeled compound (New England Nuclear Co.). The labeled choline chloride was diluted with ordinary choline chloride to bring it to a convenient specific activity of 140 $\mu$Ci/mmol. It was then dissolved in 96% ethanol and converted to the base form by adding a slight excess of silver oxide; the filtrate was then evaporated to dryness in a rotary evaporator. This procedure helped to remove most of the trimethylamine present as radioimpurity in the original choline chloride. The residue was dissolved again in 96% ethanol; to this solution was added slightly more than 1 equiv of hydrochloric acid. This was used as a stock solution and, for each experiment, an aliquot of this solution was evaporated to dryness and the residue was dissolved in the minimum amount of absolute alcohol. The latter was mixed with a large excess (usually 1:10) of chilled ($-78°$) diethyl ether. Under these conditions the choline chloride precipitates rapidly in a finely divided state. To minimize self-radiolysis, the precipitation was carried out only a few hours before use. This procedure was used for all samples, except when large crystals were needed. In the latter case, the rapid precipitation was replaced by slow crystallization from the alcohol–ether solution. In all samples there was a residual 0.1–0.2% of radioimpurity—mostly trimethylamine. This resulted principally from the effects of self-irradiation of the material during handling at room temperature.

Unless otherwise specified, all irradiations were carried out in sealed, evacuated tubes, for 1 hr, at $-196°$, in a 2000-Ci $^{60}Co$ $\gamma$-ray source at a dose rate of 2.9 Mrads ($\pm 15\%$)/hr.

The analyses for amounts of decomposition were accomplished by a chromatographic procedure, described previously,[5] applied to the $^{14}C$-labeled compound; the only difference was that, in the present work, our chromatographic solvent was *n*-BuOH–12 *N*

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[1] The work described in this paper was sponsored by the U. S. Atomic Energy Commission.

[2] B. M. Tolbert, *et al.*, *J. Amer. Chem. Soc.*, **75**, 1867 (1953).

[3] R. O. Lindblom, R. M. Lemmon, and M. Calvin, *ibid.*, **83**, 2484 (1961).

[4] R. M. Lemmon, P. K. Gordon, M. A. Parsons, and F. Mazzetti, *ibid.*, **80**, 2730 (1958).

[5] M. Ackerman and R. M. Lemmon, *J. Phys. Chem.*, **71**, 3350 (1967).

[6] I. Serlin, *Science*, **126**, 261 (1957).

[7] P. Shanley and R. L. Collin, *Radiat. Res.*, **16**, 674 (1962).

HCl-$H_2O$ (8:1:1)—a slightly different ratio from that used previously. The procedure determines, by liquid scintillation counting, the amount of trimethylamine-$^{14}C$ that appears during the radiolysis. The per cent of formation of this compound is taken as equivalent to the per cent of decomposition.

In our earlier work[3] the radiation decomposition process was allowed to proceed slowly at room temperature. To speed up this process, in the present work the post-irradiation treatment of most samples was to heat them at 50° for varying lengths of time. At this temperature the compound is still in the $\alpha$ form, but reaches its maximum decomposition in about 2 hr, instead of the several days required at room temperature.

All work with choline chloride is complicated by the compound's great hygroscopicity. Containers of the compounds were never opened except in a glove box under a dry nitrogen atmosphere. However, work in this laboratory has shown that the rigor with which the compound is dried has little effect on its radiolysis. For example, under identical conditions of irradiation and post-irradiation treatment, samples dried at 100° for 1 hr at $10^{-5}$ Torr showed almost the same decomposition as those kept at room temperature for 30 min under maximum physical contact with 0.5 Torr of water vapor.

**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 hr. 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 $\gamma$-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 $\alpha$ form's radiolysis were determined as follows. Very finely divided (to maximize surface area) choline-*methyl*-$^{14}C$ chloride was prepared by rapid precipitation from absolute ethanol solution on the addition of a large excess of 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 chloride 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 were 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 99.0% choline chloride. It was then transferred into irradiation tubes, dried at 100° for 2 hr, and irradiated as usual.

**Phototransfer of Electrons.** Samples of finely divided, $\gamma$-irradiated choline chloride were mixed with approximately equal weights of powdered Brilliant Green (bis(4-diethylaminophenyl)phenylmethane hydrochloride) or cadmium sulfide. Thin layers of one or the other mixture were sandwiched between two disks, one quartz and the other Pyrex (with a shallow well to hold the samples), and illuminated through the quartz with light from a 1000-W, GE Model A-H6, high-pressure mercury lamp, at a distance of 18 cm. During the illuminations the samples were maintained at different temperatures between −120 and 30° by passing cold $N_2$ through the chamber holding the disks. Similar experiments were carried out using 400–800-nm light, achieved with a I-69 filter between the sample and the A-H6 lamp.

**Infrared Illumination.** The possibility of detrapping electrons by infrared radiation was investigated using the same equipment, except that the mercury lamp was replaced by a 300-W tungsten lamp with a glass bulb. The lamp was 10 cm away and was focused onto the sample by means of quartz lenses.

**Effect of Different Crystal Sizes.** The sensitivity toward $\gamma$-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 long 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 $Et_2O$. To avoid the crystal-phase transition at 78°, both these samples were dried at 70°.

**Esr Studies.** The electron spin resonance spectra, and relative radical concentrations as a function of time and temperature, were determined on a Varian Model E-3 epr spectrometer. The $\gamma$-irradiations were carried out at −196° and the esr observations made at room temperature, unless otherwise noted.

**Electrical Conductivity.** Electrical conductivity measurements were made on both pelleted (10,000 kg/cm$^2$ in a hydraulic press) and unpelleted samples of choline chloride. The measurements were made in an evacuated ($\simeq 10^{-5}$ Torr) conductivity cell. Details of the cell and its use have been described by Eley and Pacini.[8]

## Results and Discussion

**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 $\gamma$-irradiation. These traps are relatively shallow and, apparently, can be depopulated completely within 2 hr at 50°. This is indicated by the fact that a maximum decomposition of 12–13% is attained in that time, and is not exceeded even if the irradiated sample is heated at higher temperatures (but below the 78° transition temperature). 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 high enough to achieve significant annealing. Prior thermal treatment at 100° also shows no effect—a possible explanation is that there is extensive 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 I.** Effect of Thermal Treatment Prior to $\gamma$-Irradiation of Choline Chloride

| Prior thermal treatment | Time of post-irradiation heating (50°)<br>30 min | <br>120 min |
|---|---|---|
| | Per cent 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%.

**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 adsorbed 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

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(8) D. D. Eley and B. M. Pacini, *Polymer*, 9, 159 (1968).

Table II. Effect of Gaseous Ambients

| Ambient | | Time of heating at 50° | |
|---|---|---|---|
| | Without heating | 20 min | 120 min |
| | Per cent 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%, except for the 120-min $I_2$ results—the latter are probably accurate only to within ±1.0%.

Table III. Radiolysis of Choline Chloride Induced by Phototransfer of Electrons from Brilliant Green and Cadmium Sulfide

| Temperature (approximate), deg | Per cent decomposition[a] | | | | |
|---|---|---|---|---|---|
| | γ-Irradiated choline chloride with Brilliant Green (1:1) | | γ-Irradiated choline chloride with cadmium sulfide (1:1) | | γ-Irradiated choline chloride without photodonors |
| | Illuminated, 4 hr | Dark, 4 hr | Illuminated, 4 hr | Dark, 4 hr | Illuminated, 4 hr |
| −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 |
| −5 | 9.7 ± 0.3[c] | 2.5 ± 0.2[c] | | | |
| 0 | 10.6 ± 0.3 | 1.4 ± 0.2[b] | | | 1.9 ± 0.1 |
| 12 | 10.5 ± 0.8 | 2.0 ± 0.2[b] | | | 2.1 ± 0.1 |
| 12 (with I-69 filter[d]) | 9.3 ± 0.4 | 2.0 ± 0.2[b] | | | 1.5 ± 0.2 |
| 30 | 12.0 ± 0.8 | 5.0 ± 0.1 | 8.5 ± 0.5 | 5.5 ± 0.5 | 5.0 ± 0.5 |
| 30 (with I-69 filter[d]) | 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. Variations in the data are, in general, higher at higher decompositions. [b] The 1.5–2% decomposition represents the radiolysis that occurs during the brief period of handling when the samples are sandwiched between the plates—at room temperature in the drybox. [c] Total γ-ray dose, 9 Mrads (instead of the usual 3). [d] Restricts illuminating light to the 400–800-nm range.

atoms, formed in small quantity during the radiolysis, also have a large affinity for electrons.

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

**Phototransfer of Electrons.** If electrons are participating in the chain decomposition, we should be able to observe radiolysis, even at temperatures sufficiently low for thermal detrapping of electrons, by phototransferring electrons from an external source. At −40°, even though the phototransfer agent is presumably providing electrons (Table III), the radiolysis chain cannot propagate. However, somewhere between −40 and −5° 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. The results obtained through the use of the phototransfer agents, Brilliant Green and cadmium sulfide, shown in Table III, strongly support the idea of an important role for electrons in the radiolysis mechanism.

**Infrared Illumination.** Illumination of the γ-irradiated choline chloride with a 300-W tungsten lamp (for 2 hr; sample temperature maintained between 5 and −5°) induced a decomposition of 1.4% (from 1.0 to 2.4). Since the A-H6 lamp, under the same conditions, does not produce an increase in decomposition (Table III, last column), one may conclude that neither visible nor uv radiation has any effect on the irradiated compound. We interpret the effect of the tungsten lamp illumination as resulting from the detrapping of electrons by the infrared radiation. However, the tungsten lamp has a glass bulb, and the intensity of the infrared may not have been sufficient for detrapping an appreciable fraction of the available electrons.

**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 hr 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 due to a lower density of defects in the large crystals and, consequently, a smaller number of donors are formed by the γ-radiation.

**Kinetics of Radical Decay and Radiolytic Decomposition.** The esr spectrum of γ-irradiated choline chloride (polycrystalline) is shown in Figure 1. This spectrum is in substantial agreement with an earlier observation of the esr spectrum of the electron-irradiated compound.[3] Observations of the spectrum during its decay showed no changes in its overall shape. Power-saturation experiments also showed that all the lines were saturated to almost the same extent. Consequently, it appears that there is only one observable free radical in the irradiated compound.

The radical decay kinetics were followed by locking the esr spectrometer on the magnetic field strength of the more intense line (marked "2nd" in Figure 1) and following the intensity of the spin signal as a function of time at 40, 50, 60, and 70°. The kinetic analysis of the data obtained at 50° is shown in Figure 2.

There appear to be three first-order components in the decay curves (Table IV). Second-order decay, due to radical–radical dimerization, is unlikely since the expected products (2,3-butanediol from $CH_3\dot{C}HOH$ or 1,4-butanediol from $\cdot CH_2CH_2OH$) have been sought but not found.[9] The three components apparently arise by

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(9) M. A. Smith and R. M. Lemmon, *J. Phys. Chem.*, **69**, 3370 (1965).

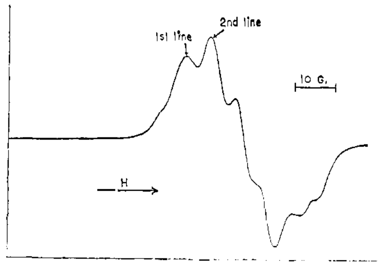

Figure 1. Esr spectrum (at ambient temperature) of γ-irradiated (1 hr, −196°, 2 × $10^6$ rads) polycrystalline choline chloride.

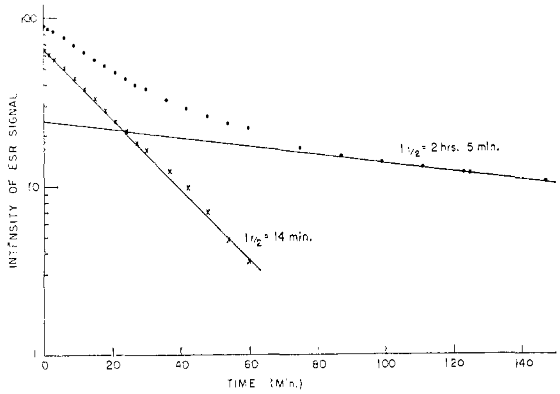

Figure 2. First-order components in the decay kinetics at 50° of the second line of the esr signal in γ-irradiated choline chloride.

virtue of depopulation of electrons from three donors with different depths—the detrapped electrons then interact with radicals that initiate the chain decomposition. An Arrhenius plot gave the activation energy of the fastest decaying component to be approximately 0.9 eV. This we presume to be the energy necessary to detrap electrons from the shallowest donor level. The third component could arise from electrons depopulating from the valence band or a deep donor.

Table IV. Radical Decay and Radiolytic Decomposition Half-times

| | Radical decay[a] | | | Thermal decomposition | |
|---|---|---|---|---|---|
| | Component | | | Component | |
| Temp deg | First | Second | Third | First | Second |
| 40 | 14 min | 14 min | Very slow | | |
| 50 | 4.5 min | 14.5 min | Very slow | 6 min | 37 min |
| 60 | 2.6 min | 13.5 min | [b] | | |
| 70 | 52 sec | [b] | [b] | | |

[a] Because of the lack of data on the very slow third component, all these figures must be considered only approximate. [b] Kinetics not followed.

The kinetics of radiolysis at 50° of the γ-irradiated compound were determined (see Figure 3) and these are to be compared with the radical decay kinetics at the same temperature (Figure 2). If the decay of radicals (which are chain initiators) is taking place entirely due to radical–electron interactions, and if there is no competing mechanism for radical disappearance, one would expect correspondence between the kinetics of radiolysis and of radical decay. However, the correspondence is not good with respect to the slower component (Figures 2 and 3 and Table IV). We believe that this lack of correspondence is due mainly to a decrease in the decomposition chain length with increasing decomposition. Therefore, the chain length varies with time. This explains shorter half-times for radical decay as compared to thermal decomposition half-times.

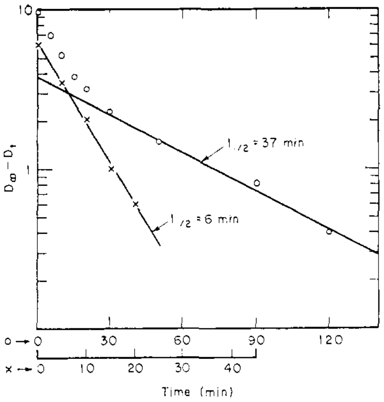

Figure 3. First-order components in the decay kinetics of thermal decomposition at 50° of γ-irradiated choline chloride. (The ordinate is saturation decomposition minus the decomposition at time $t$.)

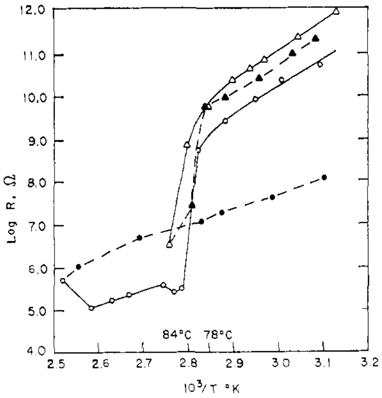

Figure 4. Electrical conductivity of choline chloride: (○) pellet 1, heating; (●) pellet 1, cooling; (△) pellet 2, heating; (▲) pellet 2, cooling.

**Electrical Conductivity.** The conductivity data for for the pelleted choline chloride are shown in Figure 4. 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 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 4 (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 Figure 4). Such large increases in conductivity at the phase-transition region have not hitherto been reported, though an increase of an order of magnitude has been observed in polycrystalline chloropromazine.[10] Conductivity in the α form appears to be mainly electronic, while in the β form it is probably protonic, as we

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(10) F. Gutman and L. E. Lyons, "Organic Semiconductors," Wiley, New York, N. Y., 1967, pp 531-532.

observed marked polarization effects and significant nonlinear current–voltage characteristics. The $\beta$ form has a highly disordered crystal structure[11] and has sufficient room for rotation about a number of equilibrium positions. Protonic conductivity necessarily means easy intermolecular transfer of protons through hydrogen bonds. It may be that this high proton mobility saves the $\beta$ form from the radiolysis that the $\alpha$ form undergoes. (In the $\alpha$ form's radiolysis there is little evidence of intermolecular transfers.[12] If the $\gamma$-irradiated $\alpha$ form is heated above 78°, little ($<1\%$) radiolysis occurs. We believe that this means that the free protons, rather than electrons, are reacting with the radicals. In this way, the initiation of chain decomposition, resulting from an electron–radical interaction, is prevented.

**Cyclic Experiments.** Aliquots of choline chloride were subjected to repeated cycles of $\gamma$-irradiation and heating at 50°. The per cent decomposition was compared in each case with that of an aliquot subjected to the same dose of $\gamma$-irradiation (in a single irradiation), followed by heating. For example, in a five-cycle experiment the samples were subjected to 1 hr of $\gamma$-irradiation followed by heating at 50° for 2 hr; this was repeated five times, and the per cent decomposition was compared with that from 5 hr of steady $\gamma$-irradiation followed by 10 hr of steady heating at 50°. The latter data are shown in Table V under the heading "continuous," while the former are shown under the heading "intermittent."

**Table V.** Effects of Repeated Cycles of Irradiation and Heating

| No. of cycles | Per cent decomposition<br>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 hr, the maximum radiolysis attained in a single cycle does not exceed 13%. A similar observation was made in the case of the phototransfer experiments (Table III). It is also interesting to note (Figure 3) that almost 50% of the decomposition occurs in the first 10 min of heating at 50° and 90% in 60 min. Again, the radiolysis half-times (especially for the second component) are much longer than that of radical decay (Table IV). 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. Preliminary experiments have shown that the post-irradiation thermal treatment yields lower decomposition in an ambient of acetaldehyde. 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 hr, the dominant process seems to be the diffusion of acetaldehyde to the surface of the microcrystallites. Consequently, if this heated material is $\gamma$-irradiated again, the initial stages of the second post-irradiation thermal treatment would involve much longer chain lengths than the heating during the latter half of the 2-hr 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% 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.

## Summary and Conclusions

The radiation damage in crystalline choline chloride can be deferred indefinitely by irradiating and storing at low temperatures. The damage, however, develops rapidly at 50°. The radiolytic decomposition is retarded in electron-accepting ambients of $O_2$, $SF_6$, $N_2O$, and $I_2$. Radiolysis can also be induced at lower temperatures in $\gamma$-irradiated choline chloride by (1) the phototransfer of electrons from Brilliant Green and cadmium sulfide and (2) photodetrapping of electrons from donors by infrared illumination. These observations can be interpreted on the basis of the following model.

(A) Electrons are trapped during irradiation, on either preexisting crystal defects or ones created during irradiation, to form donors. During post-irradiation thermal treatment, the electrons are thermally released from the donors and react with radicals (which are chain initiating) to form excited species that participate in self-propagating chains.

(B) The kinetics of both radical decay and radiolytic decomposition are primarily governed by two first-order components—a third, very slow component may arise by a small depopulation of electrons from the valence band or a deep donor. The rate of radiolytic decomposition is slower than radical decay, especially at later stages of thermal treatment. This indicates that the chain length diminishes markedly, presumably owing to buildup of the chain terminator, acetaldehyde, as radiolysis progresses. Additional support for this suggestion is obtained from the following observations. (a) The radiolytic decomposition is retarded in an ambient of acetaldehyde. (b) Aliquots of choline chloride subjected to repeated cycles of $\gamma$-irradiation and thermal treatment at 50° yield much higher radiolytic decomposition than ones which have been given the same integrated dose and thermal treatment in a single cycle (Table V). In the case of multiple cycles, the radiolytic product, acetaldehyde, diffuses to the surface of the microcrystallites during each cycle of *prolonged* thermal treatment at 50°, thereby enhancing the chain length for the postirradiation thermal treatment of the subsequent cycle.

(C) The high-temperature $\beta$ polymorph exhibits a very much larger conductance than the $\alpha$ form. Appreciable nonohmic and polarization effects are also observed for the $\beta$ form, which are strongly suggestive of protonic conductivity. The large dominance of protonic over electronic conductivity in the $\beta$ form may also account for its radiation stability. The protons can interact with the radicals before electrons get a chance to do so, and thus inhibit chain propagation.

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(11) R. L. Collin, *J. Amer. Chem. Soc.*, **79**, 6086 (1957).

(12) R. M. Lemmon and M. A. Smith, *ibid.*, **85**, 1395 (1963).