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Further Studies on the Solid-State Chemistry of Irradiated Choline Chloride[1]

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Abstract: The remarkable radiation sensitivity of crystalline choline chloride has been investigated by studies of infrared and esr spectra, photochemical transformation of radicals, microwave electrodeless conductivity, and exposure to hydrogen atoms, vacuum ultraviolet, and thermal electrons. These studies lend support to the involvement of both ethanol radicals and electrons in the chain decomposition. They also show that hydrogen atoms can induce the decomposition. These observations indicate that during subsequent thermal treatment of γ-irradiated choline chloride, the detrapped electrons interact with ethanol radicals to form hydrogen atoms, which propagate the chain decomposition.

Previous papers in this series[3,4] have reported solid-state studies on the unique radiation sensitivity of a particular crystal form (α) of the common, and biologically important, salt choline chloride, $[(CH_3)_3NCH_2CH_2OH]^+Cl^-$. The essence of the problem under investigation may be stated in these two questions: (1) Why is this particular quaternary ammonium salt so radiation labile whereas its closely related chemical analogs show normal behavior towards ionizing radiation?

(2) Why is a particular polymorph (α) of choline chloride labile, whereas another (β) is radiation-normal?

The present work was directed towards a probing of the differences in physical properties between radiation labile and resistant forms. Our probes have been the infrared spectra, esr spectra, and electrodeless conductivity measurements. In addition, we have observed the photochemical transformation of the radiation-produced radicals in the α form, and the effects of thermal electrons and hydrogen atoms on that form's radiolysis. The hydrogen atom work, together with previous observations, indicates a role for hydrogen atoms in the radiation decomposition. This role is included in the mechanism that we now propose for the radiolysis.

Experimental Section

Our sources of choline chloride and its analogs, the purification procedures, the methods to determine the extent of radiolysis, irradiation techniques, and general laboratory procedures have been described previously.[3,5,6]

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 deliquiscent choline chloride crystals. The solid mixture is then further dried on a vacuum line (10^{-4} Torr at 100° for 2 hr). The dried samples are sandwiched between KBr powder in a metal die 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 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.[5]

The esr spectra, and changes in radical concentrations, were determined on a Varian Model E-3 spectrometer equipped with a variable temperature assembly. The effects of UV illumination on the radical concentrations in γ-irradiated choline chloride were determined by sandwiching a few mg of the irradiated compound between quartz and brass plates. The choline was illuminated thru the quartz with a G.E. AH-6, high-pressure mercury lamp, at a distance of 18 cm, for 4 hr. 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.

The electrodeless conductivity measurements were made in a bimodal cavity resonating at 9.5 GHz; the equipment and techniques have been previously described.[7,8] We used the choline chloride in the form of a pellet, 3 mm in diameter and 0.5 mm thick, compressed at 10,000 Kgm/cm^2. To avoid moisture absorption, the pellet was sealed between very thin films of polyester before being placed in the cavity. The heating of the pellet in that position was accomplished by passing a stream of preheated nitrogen thru the cavity. Its temperature was measured by a thermocouple.

Thermal electrons were injected into choline chloride samples by means of corona discharge equipment that has been described previously.[9]

The electrons were transported in an argon stream, and cooled to thermal equilibrium by the admixture of 1% of CO_2 into the argon. Samples of choline chloride were exposed to the current of thermal electrons of about 2 μamp for 1-2 hr. The voltage varied from 5 to 8 kV.

Hydrogen-atom irradiations were performed at ambient temperature on the apparatus shown in Figure 1. The "light trap" was used to avoid simultaneous illumination of the sample with the vacuum-UV light from the excited hydrogen. When we wished to observe vacuum UV effects on choline, we removed the light trap and replaced it with the choline mounted vertically on a glass receptacle; in this way the choline faced directly toward the excited hydrogen in the microwave cavity. We also pumped off the hydrogen atoms thru a connecting "tee" placed between the choline and the microwave cavity. (Experience with this arrangement--for example, failure to produce radicals in malonic acid--showed that hydrogen atoms were not reaching the sample.) The microwave power (2450 MHz) was supplied by a Litton Industries model L-3189 magnetron.

Results and Discussion

Infrared spectra. Figure 2, a and b, shows the infrared spectra of choline chloride in its α and β forms respectively. It can be seen that there are some differences between the two. When the β form is cooled back thru the 78° transition point the spectrum returns to exactly what it was (α form spectrum) before the heating to above 78°. This same complete reversal to the low temperature form was also observed for all the choline analogs discussed below.

Assignments of the peaks labeled in Figure 2a were made on the basis of the infrared spectra of selectively deuterium-labeled choline

chloride. 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.

Differences in the $O-CH_2$ peaks are among the major ones noted between the α and β spectra. 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 $[(CH_3)_3NCH_2CD_2OH]^+Cl^-$, α form, is less than half as radiation sensitive as the α form of ordinary (fully protonated) choline chloride.[10] 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 a hydrogen atom out of the $O-CH_2$ group is a key process in the radiolysis--and both intramolecular and some intermolecular transfers of these hydrogens have been shown by previous studies.[11]

In our present studies we also observed the infrared spectra of choline bromide, choline iodide, and of the "chloro analog," $[(CH_3)_3NCH_2CH_2Cl]^+Cl^-$. Our measurements of the change of electrical conductivity with temperature have indicated that these compounds also exist in low- and high-temperature polymorphs--the bromide transition being at 91°, the iodide at 94°, and the chloro analog at 137°. 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.[12] On the other hand, the spectra of the iodide and of the chloro analog, which show no anomolous radiation sensitivity, are considerably different from those of the chloride and bromide.

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.[13] The stretching frequency for the choline compounds (all of those studied here) occurs 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.[14]

We have also compared the infrared spectra of ordinary choline chloride (α form) and the irradiated (5 Mrads), but not yet decomposed, compound. There were no detectable differences in these spectra.

Esr spectra. Much work has been done previously on the esr spectrum (at ambient temperature) of γ-irradiated choline chloride.[4,5] That work showed a predominantly 5-line spectrum that was attributed to an ethanol radical, $\cdot CH_2CH_2OH$. The same radical spectrum is found in irradiated choline bromide. We have also examined the spectra of irradiated choline iodide, choline sulfate, $[(CH_3)_3NCH_2CH_2Cl]^+Cl^-$, $[(CH_3)_3NCH_2CH_2CH_2OH]^+Cl^-$, and $[(C_2H_5)_3NCH_2CH_2OH]^+Cl^-$. The spectra of these five compounds are completely different from that of the radiation-sensitive chloride and bromide. A detailed analysis of their spectra was not attempted; however, it is clear that the radicals formed in all analogs except choline chloride and choline bromide are not ethanol radicals. It appears that this particular radical must be present for the propagation of the chain radiolysis.

Photochemical transformation of ethanol radicals in γ-irradiated choline chloride. Esr spectra for a control, non-illuminated sample and that for an illuminated specimen are shown in Figure 3; both spectra were taken at ambient temperature. The control sample had been maintained at that temperature, as well as at -20°, for the same length of time as the illuminated one during the sandwiching, etc. 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 photo-transformation of the ethanol radical. The presence of the new radical is shown by the new peak marked "1" in Figure 3(b). It is also observed that the peak marked "2" has been shifted to higher fields compared to what it was in the unilluminated sample (Figure 3(a)). When the illuminated sample is heated for 2 hr at 70°, the ethanol radical completely decays and only the photo-transformed radical is observed (Figure 4). (Heating at 70° for 2 hr, without previous illumination, leads to the loss of all radical signal.) This radical is relatively stable and the signal further decays, over 16 hr at 70°, to about 2/3 of the original value. Since the radiolysis reaches its "saturation" value in only a few minutes at that temperature,[4] it is obvious that this new radical plays no part in the chain decomposition.

According to our model proposed earlier[3], free electrons interact with ethanol radicals to form a reactive species that initiates 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 irradiatedd (5 Mrads), illuminated (4 hr at -20°) samples of choline chloride are approximately 4.8% decomposed on subsequent thermal treatment (90 min at 50°). On the other hand, samples treated exactly the same way, except kept unilluminated for 4 hr at -20°, showed approximately 7.6% decomposition. The photo-treatment reduces both the ethanol radical concentration and the subsequent radiolysis. Therefore, the involvement of the ethanol radical in the radiolysis has been directly demonstrated.

We also made some efforts to determine the wavelength dependence of the photochemical transformation of the ethanol radicals. This was done by interposing Corning filters 7-54, 4-71, and 3-69 between the AH-6 lamp and the choline chloride samples. These filters transmit in the approximate wavelengths of 250-400, 350-570, and 530-1000 nm respectively. When either the 4-71 or 3-69 filter was used, the radical decay was the same as when the sample was not illuminated, and no new radicals were formed. The use of the 7-54 filter led to a reduction of the ethanol radical's intensity by a factor of 3 (the unfiltered illumination gave a reduction of 10), and the new radical's intensity was about the same as in the unfiltered illumination. This suggests that the decay of ethanol radicals takes place within the 200-350 nm range (the shorter wavelengths being the more effective), while the formation of the new radical takes place between 250 and 350 nm. The decay of the radicals might also result from (a) detrapping of electrons by the

ultraviolet light and/or (b) the competing photolysis: $\cdot CH_2CH_2OH \xrightarrow{h\nu} CH_3CHO + \cdot H$.

The photo-detrapping of electrons is also expected to occur in longer wavelength regions--about 2 eV or 600 nm--as indicated by our earlier thermoluminescence studies[4]. However, we have found that illumination of irradiated choline chloride with >400 nm light (Corning 3-73 filter)) has no effect on either the radical decay or the subsequent radiolysis. This failure may be due to the greater scattering of the visible light from crystal surfaces, and little penetration of the light into the interior of the crystals.

Electrical conductivity measurements. The direct-current conductivity measurements of polycrystalline choline chloride were reported earlier.[3] It was found that the conductivity increases sharply by four orders of magnitude at 78°, the temperature at which choline chloride undergoes crystal phase transformation. Also, the high temperature polymorph (β form) decomposes under the stress of applied voltage and shows marked electrical polarization and non-ohmic behavior. On the basis of these results it was proposed that the charge carriers in the β form may be protons as compared to electrons in the low temperature polymorph (α form).

Due to inter-surface barriers in polycrystalline materials and possible charge injections from the electrodes, the results obtained from d.c. conductivity measurements are open to question. Therefore, we decided to do electrodeless conductivity measurements at microwave frequencies (9.5 GHz). At these frequencies inter-surface barriers do not play any significant role. In addition, the sign and mobility of charge

carriers can be measured independently. The general procedure and theory have been described.[7,8,15]

The microwave absorption measurements showed a sharp increase in conductivity as one goes from the α to the β form. 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 effectively as we could in the d.c. measurements. Moisture does increase d.c. conductivity of the α form significantly while not having much effect on 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. Furthermore, conductivities tend to be greater in these a.c. measurements because of the removal of the effects of inter-surface barriers in polycrystalline materials.

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

$$\frac{\Delta Q}{Q} = K_1 \sigma \frac{V_s}{V_c} \quad \text{and} \quad \Delta P = K_2 \frac{\Delta Q}{Q} \mu H$$

where ΔQ is the difference in Q between the loaded and empty cavity,[16] σ is conductivity in the sample, V_s and V_c are volumes of sample and cavity respectively, ΔP is the change in power upon the application of magnetic field H, and μ is the mobility of charge carriers in the sample.

As the equations indicate, the experimentally measured quantity ΔP will be very small, for low conductivity materials, unless the sample size is large. This size cannot be increased indefinitely due to difficulties of a large decrease in Q, and in the tuning of the cavity. Also, the assumptions used to derive the above equations, such as non-distortion of fields in the cavity, will no longer be valid.

Choline chloride in the α form has a small conductivity and, therefore, a compromise was made for the size of the sample. It was found that the mobilities of the charge carriers in the α form are at least an order of magnitude larger than those of the 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[17] in the β form was too low for us to measure it, or to determine the sign. The mobility in the α form varied from -0.3 to -1.0 cm^2/volt-sec. The low mobility of charge carriers in the β form indicates ionic carriers. This agrees with the previous proposal of protonic carriers in the β form.[3]

Effects of thermal electrons. Exposure of finely-divided choline chloride samples to thermal electrons led to no detectable esr signal, to no observable thermoluminescence,[18] or to any change in the rate of decay of the ethanol radicals in previously γ-irradiated samples. Attempts to increase the time of exposure of samples to the electrons were unsuccessful because, after 1-2 hr exposure, enough charge builds up on the sample to prevent any further flow of electrons.

However, we did find that the injection of these thermal electrons into previously vacuum-UV illuminated choline chloride led to a small, but definite increase in decomposition. Exposure of choline chloride to the vacuum ultraviolet illumination produces ethanol radicals and presumably leads to chain decomposition (see below). The UV-exposed samples were subjected to the thermal electron injection at room temperature for 2 hr. Controls were also exposed to the UV, but not to the thermal electrons. The electron exposed samples showed 0.35% decomposition, the controls 0.15%. Another set of samples was treated exactly as above,

except that they were additionally heated at 50° for 2 hr. The decomposition for electron injected samples was 0.80%, compared to 0.45% for controls.

These observations provide direct evidence for the involvement of electrons in the chain decomposition. The effect is small because we have been able to inject only a limited number of thermal electrons. The enhancement of the effect at 50° shows that a fraction of the electrons are trapped during the room-temperature exposure to the thermal electrons.

Effects of hydrogen-atom and vacuum-UV irradiations. Although we have made no direct determinations of the hydrogen-atom fluxes obtained in the apparatus shown in Figure 1, we monitored the apparatus' performance by occasionally substituting malonic acid for the choline chloride. This gave us the strong, 2-line esr spectrum that has been previously reported for H-atom irradiated malonic acid,[19] and that has been attributed to the radical $\dot{H}C(CO_2H)_2$.

Irradiation of choline chloride with hydrogen atoms led to no observable esr signal, even when the exposures to the atoms, and the subsequent esr observations, were done at low temperature (<-20°). This result is ascribable to the greater ease of abstraction of hydrogen atoms from the malonic acid's α carbon than from any position on the choline cation. However, H-atom irradiations do induce chain decomposition in choline chloride. Depending on the length of H atom exposure we have found (without any subsequent thermal treatment) as much as 9% decomposition. Since the hydrogen atoms will have limited range, their effects will be primarily confined to the surface, and this amount of decomposition

indicates an important role for these atoms in the decomposition mechanism. A feature of the H atom-induced reactions that is quite different from the γ radiolyses is the appearance of much polymeric product--with yields even higher than those of trimethylamine. This effect is probably also related to the greater density of reactive intermediates at the surface in the H atom irradiations.

On illumination of choline chloride by vacuum UV light (removal of the "light trap" of Figure 1) we observed a weak ethanol-radical esr signal, and a few tenths of a percent of decomposition. It is apparent that this light, the emission spectrum of H_2, affects choline chloride in a manner very similar to that of γ-rays. The greater effectiveness of the latter probably lies in their ability to penetrate into the interior of crystals, and in their capability of creating a larger density of electron donors.

Proposed mechanism. Following some of our earlier studies[3] we proposed that the following processes take place in γ-irradiated choline chloride: The electrons resulting from the ionizing events are trapped on preexisting crystal defects and possibly on those created during irradiation. These electrons (donors) can be thermally detrapped, and the free electrons can react with ethanol radicals to form some energy-rich species that participate in self-propagating decomposition chains.

In the present work, we have found further evidence for the involvement of ethanol radicals: (a) Observations made on other γ-irradiated choline derivatives showed that ethanol radicals are produced only in choline chloride and choline bromide--and these are the only choline salts, or analogs, that are known to be abnormally radiation sensitive (i.e., show chain decomposition). (b) Low-temperature photochemical transformation of the ethanol

radicals results in a considerable diminution of radiolysis during subsequent thermal (50°) treatment.

In the present work, we have also found further direct evidence for the involvement of electrons in the chain propagation. Vacuum-UV illuminated (i.e., ethanol-radical containing) samples show an enhanced decomposition if these samples are also exposed to thermal electrons. The involvement of electrons is also supported by microwave-frequency conductivity measurements. These investigations indicate that the charge carriers in the α (radiation-sensitive) form are electrons, and that those in the β (radiation-stable) form are ions, and are probably protons.[3] We believe that the β form's stability results from the reaction of protons with ethanol radicals, resulting in the radicals' destruction before electrons can interact with them and cause the chain decomposition.

We have considered the question of the identity of the "excited" species that seems to result from the electron-ethanol radical interaction. Since H atoms cause considerable decomposition of choline chloride, we suppose that the "excited" species give H atoms and that the latter are causing this chain decomposition (reactions 5a and 6 of the following overall mechanism):

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

(1b) $(CH_3)_3\overset{+}{N}CH_2CH_2OH \rightsquigarrow (CH_3)_3\overset{+}{N}CH_2CH_2OH^*$

(2) $(CH_3)_3\overset{+}{N}CH_2CH_2OH^* \longrightarrow (CH_3)_3\overset{+}{N}\cdot\cdot CH_2CH_2OH$

(3) $(CH_3)_3\overset{+}{N}\cdot\cdot CH_2CH_2OH \longrightarrow (CH_3)_3\overset{+}{N}\cdot + \cdot CH_2CH_2OH$

(4) $\bullet CH_2CH_2OH + \underset{\text{(detrapped)}}{e^-} \longrightarrow [:CH_2CH_2OH^*]^-$

(5a) $[:CH_2CH_2OH^*]^- \longrightarrow CH_3CHO + H\cdot + e^-$

(5b) $e^- + (CH_3)_3\overset{+}{N}CH_2CH_2\overset{+}{O}H \longrightarrow (CH_3)_3\overset{+}{N}CH_2CH_2OH + h\nu$
(hole)

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

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

Overall reaction:

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

The above mechanism accounts for the appearance of trapped electrons and holes (reaction 1a) and of biradicals[4] (reaction 2). Subsequent separation of the biradical into two monoradicals[4] is shown in reaction 3. The role of detrapped electrons is indicated in reaction 4, the source of the H atoms in reaction 5a, and the chain propagation in reaction 6. The driving force for this chain propagation would be the difference between the N-H and N-C covalent bond energies (approx. 84 and 49 Kcal/mole respectively). Reaction 7 would end the chain. For simplicity, the chloride ion has been omitted from these reactions, although its presence would be important in stabilizing the "hole" shown in reactions 1a and 5b.

Our failure, in spite of some effort, to find the $(CH_3)_3\overset{+}{N}\cdot$ radical in irradiated choline chloride we ascribe to excessive broadening by the nine protons and to very rapid spin-lattice relaxation times. However, as reported by Symons,[20] and confirmed by us, this radical is easily found in irradiated trimethylamine hydrochloride. It should be emphasized that our ethanol-radical's esr spectrum (Fig. 3a) is not simple, and small amounts of other paramagnetic species, such as trapped electrons and holes, may also be present.

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(16) Q, the "quality factor of a resonator," is associated with microwave power losses due to the conductivity of the metal walls of the cavity.

(17) Given by $\mu = e\tau/m^*$, where τ is the relaxation time and m^* is the effective mass of the carriers of charge e..

(18) Our techniques for observing thermoluminescence are given in reference 4.

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Figure Captions

Figure 1. Apparatus used to expose samples to H atoms or (with the light trap removed) to vacuum UV.

Figure 2. Infrared spectra of the α form of crystalline choline chloride (a) and of the β form (b): The peak assignments are based on the spectra of selectively deuterated choline chlorides.

Figure 3. Esr spectra, at 22°, of γ-irradiated, unilluminated choline chloride (a), and of γ-irradiated, illuminated choline chloride (b).

Figure 4. Esr spectrum, at 22°, of irradiated, illuminated choline chloride after heating at 70° for 2 hr.

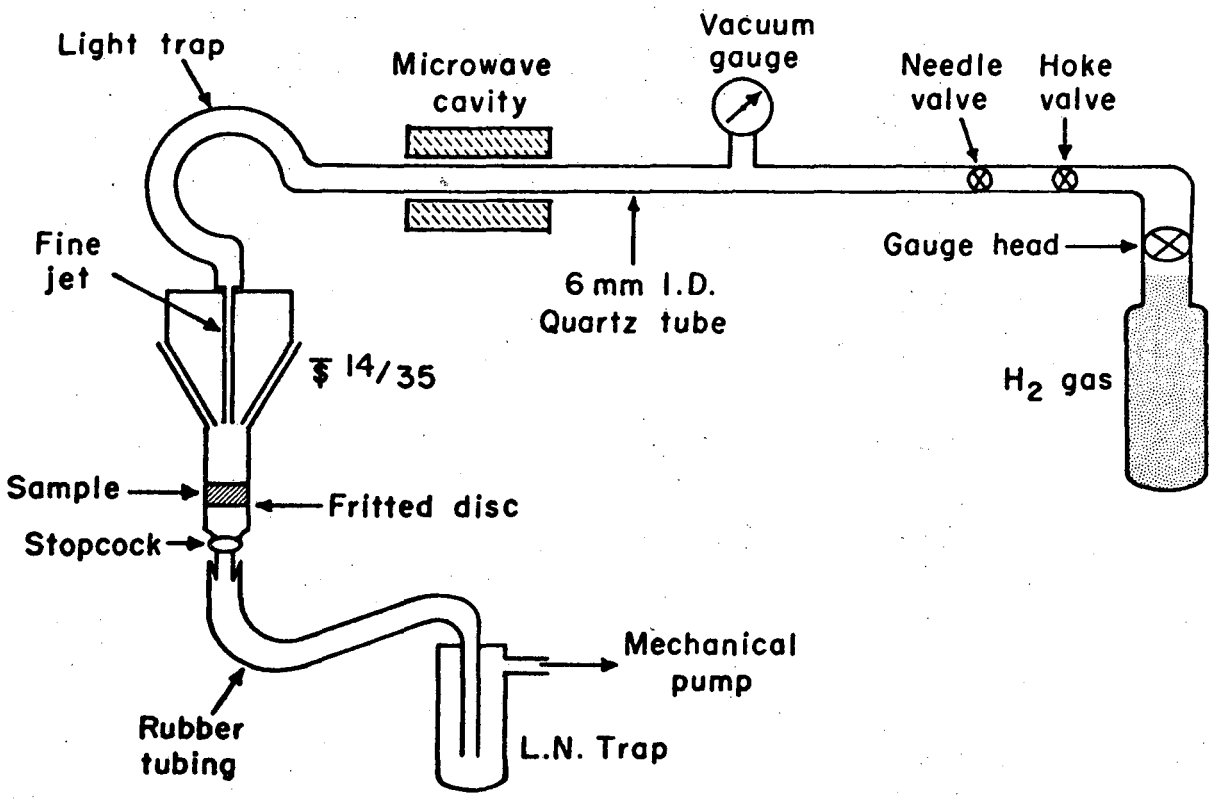

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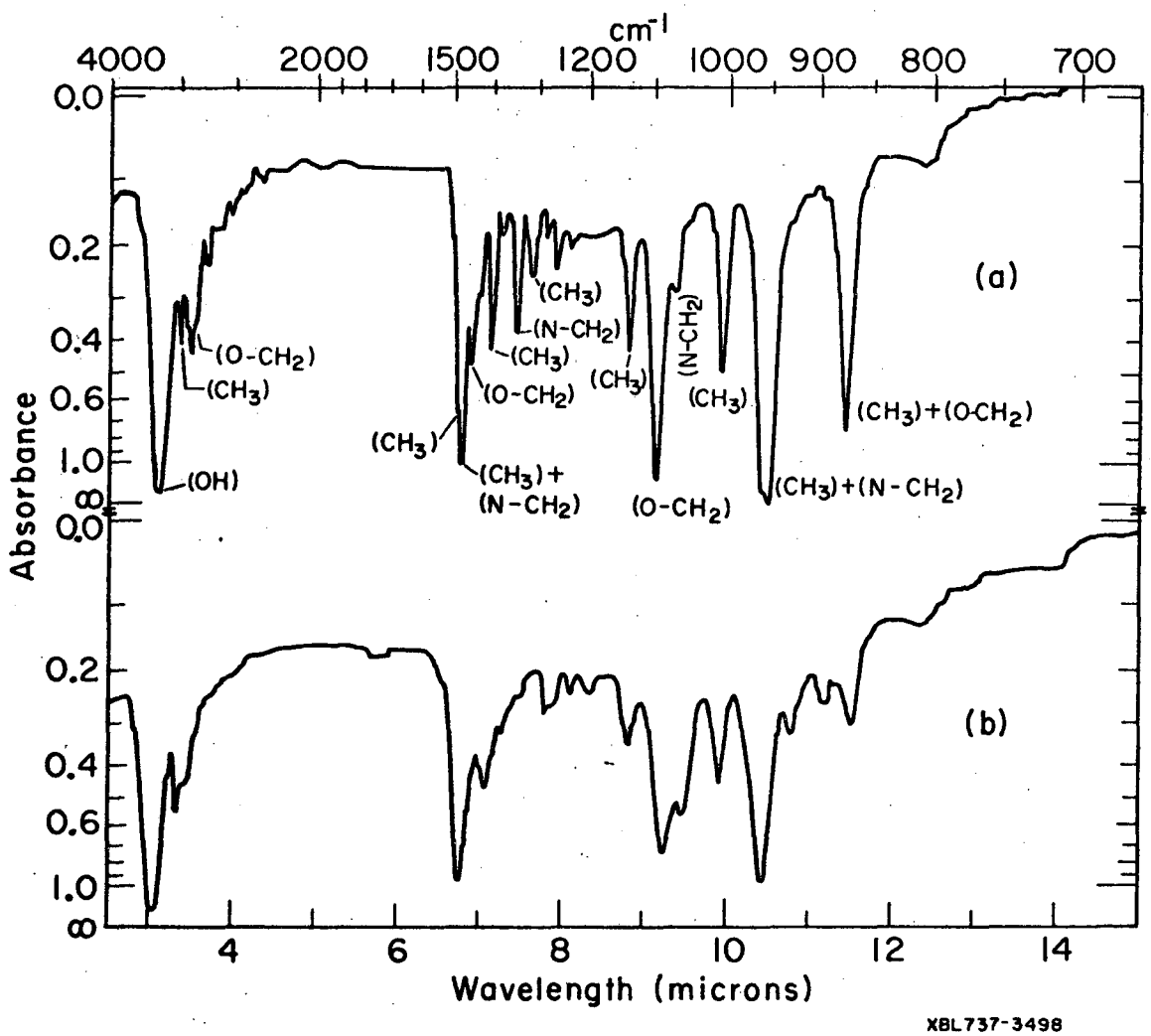
Fig. 1


cm⁻¹
4000
2000
1500
1200
1000
900
800
700
0.0
0.2
0.4
0.6
1.0
∞
Absorbance
(a)
(b)
(OH)
(O-CH2)
(CH3)
(CH3)
(CH3)+
(N-CH2)
(O-CH2)
(CH3)
(N-CH2)
(CH3)
(CH3)
(O-CH2)
(N-CH2)
(CH3)
(CH3)+(N-CH2)
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8
10
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14
Wavelength (microns)
XBL737-3498

Fig. 2

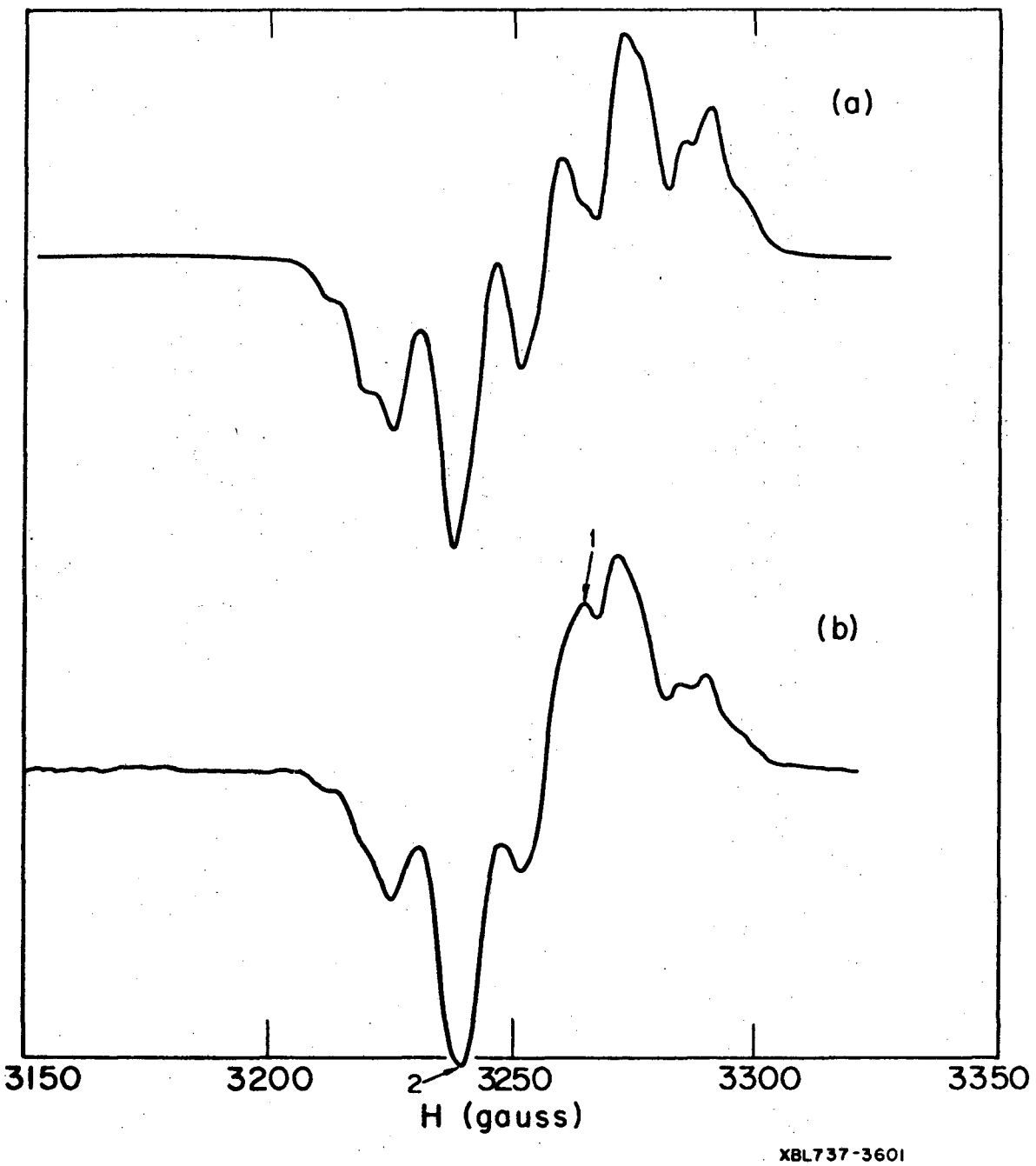
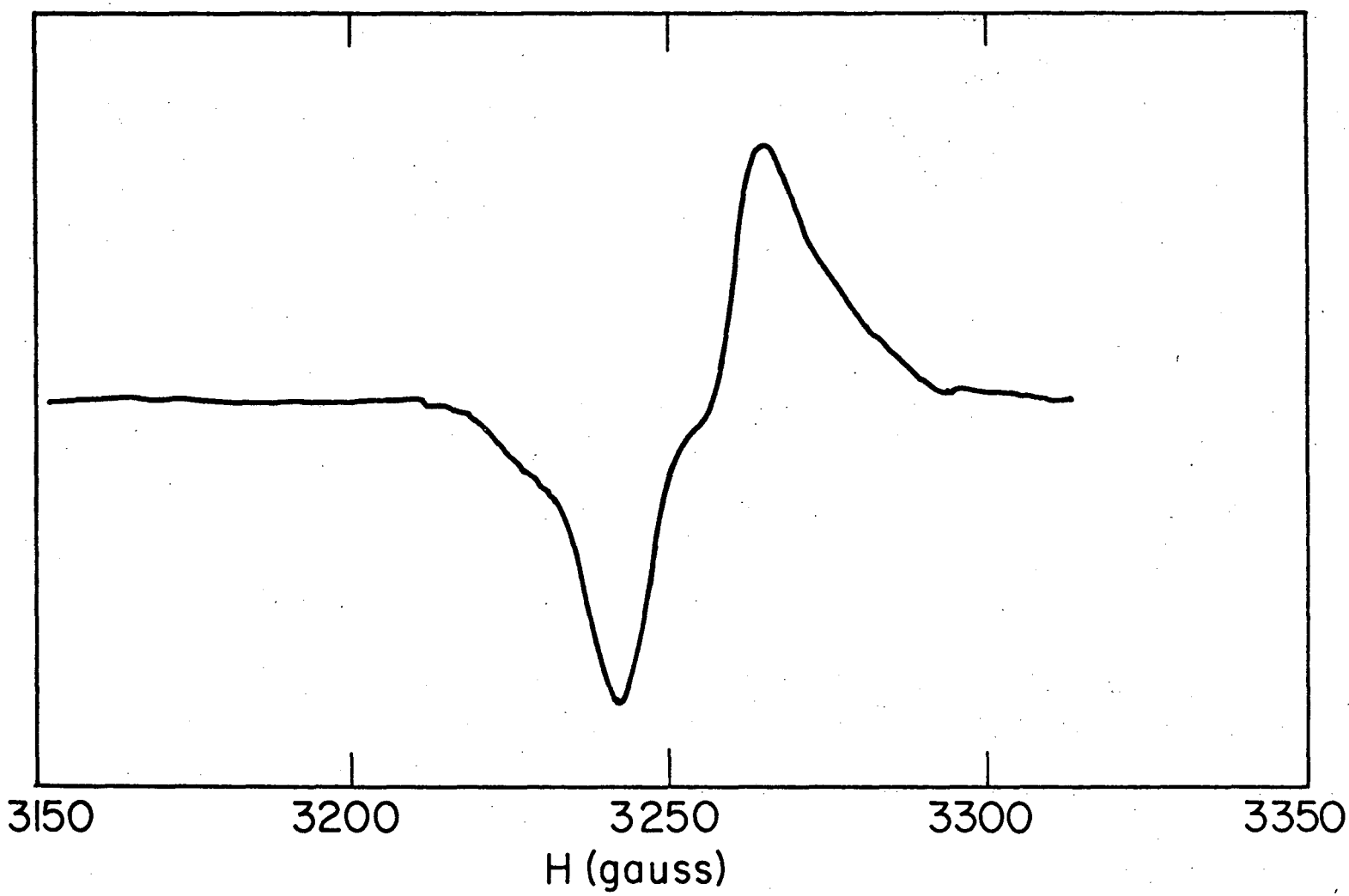


Fig. 3



XBL737-3600

Fig. 4

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