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PRODUCT INVENTORY IN THE RADIOLYSIS OF CRYSTALLINE CHOLINE CHLORIDE¹

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A quantitative study was made of all detectable products that appear when the extraordinarily radiation-sensitive organic crystal, choline chloride, was exposed to γ radiation. Besides the known major products, trimethylamine and acetaldehyde, only trace amounts of other products (H_2 , CH_4 , CH_3Cl , Cl_2 , crotonaldehyde, and paraldehyde) are detectable. The total yield of these trace products is not more than 3% of the decomposed crystal. These results emphasize the very specific nature of the radiolysis mechanism.

The earliest report of the unique radiation sensitivity of crystalline choline chloride indicated that the identified radiolysis products, trimethylamine and acetaldehyde, accounted for essentially all the decomposed choline.² However, that indication was provided principally by paper chromatographic studies of non-volatile products. The present study, which includes quantitative measurements of all detectable products, was undertaken in the hope that a full product inventory would shed further light on this unique radiolysis mechanism.

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

(2) B. M. Tolbert, et al., J. Am. Chem. Soc., 75, 1867 (1953).

Experimental Section

Sample Preparation and Irradiation. The unlabeled choline chloride used was the Eastman Organic Chemicals "white label" product. The ^{14}C -methyl labeled compound was prepared by reacting $^{14}\text{CH}_3\text{I}$ with dimethylaminoethanol; the resultant iodide was converted to chloride by treatment with Ag_2O followed by HCl . The labeled chloride was recrystallized from ethanol-ether.

Fourteen-mm. O.D. Pyrex tubes fitted with a break seal were each charged with 133 mg. of choline chloride dissolved in 0.5 ml. of methanol. After the bulk of the methanol was evaporated under a stream of dry nitrogen, the tubes were placed in an ice-salt bath and connected to a vacuum line. The samples were evacuated very slowly and pumping was continued for approximately 24 hr. while the cooling bath was allowed to warm to room temperature. The samples were then heated to 100° for 30 min., and the tubes sealed. By means of a 3000 curie ^{60}Co source, the samples were given a total dose of from 28 to 192 Mrads at a rate of 11.6×10^5 rads/hr. In order to look for a dose rate effect, in one experiment (5) the dose rate was increased to 116×10^5 rads/hr.

Determination of Hydrogen, Methane, and Acetaldehyde. The irradiated samples were connected to a vacuum system of known volume fitted with a Zimmerli pressure gauge and two traps. The first trap served both as a collector of volatile products and as a reservoir for the ethanol used to dissolve the crystalline sample. The second trap was packed with a 4A molecular sieve (Linde). Preliminary work

with this sieve (200-500 mg.) had shown that a 1 cc. sample of methane injected into the system with a gas-tight syringe was totally absorbed at -196° , and was not released even after evacuation of the trap to a pressure of 10 microns for 20 min. (Carbon monoxide is known to be even more strongly bonded to the molecular sieve.) However, subsequent heating to 150° for a few minutes gave 100% recovery of the methane from the sieve.

After 250 μ l of ethanol solvent was frozen in the first trap, the entire system was thoroughly evacuated. The sieve trap and the Zimmerli gauge were closed and the sample tube opened after it had been cooled with liquid N_2 (to prevent any sudden release of gaseous products that might carry some solid sample out of the tube) and then allowed to come to room temperature. The volatile products were distilled into the first trap, which was held at -196° . The sieve trap was cooled to -196° , opened, and 20 min. allowed for the transfer of volatile compounds (only CH_4 was subsequently seen on the gas chromatograph) from the first trap to the sieve. Following this transfer, the Zimmerli gauge was opened and the pressure of H_2 read. The H_2 was then pumped off, the sieve trap closed, and the contents of the first trap distilled into the sample tube in order to dissolve the crystalline sample. After the sample was in solution, all the volatile material was again distilled into the first trap. The transfer of methane into the sieve trap and the determination of H_2 pressure was repeated (no further H_2 was observed).

The sieve trap was connected to the injection port of a Varian Aerograph Model A-350 gas liquid chromatograph. After the trap was

heated to 200°, the contents were injected onto a 4-ft., 0.25-in. 5A molecular sieve column maintained at 80°; He flow rate (F) 30 cc./min. (Only CH₄, retention time [t_R] 16 min., was detected.) The first trap was packed in dry ice, transferred to a dry box, and opened. The contents were drawn into a syringe which had been cooled in dry ice, then quickly injected into the A-350 and chromatographed on a 20-ft., 0.25-in. column of 30% "UCON Polar" on acid- and dimethylchlorosilane-treated 45/60 mesh Chromosorb W (He F 30 cc./min., temp. 70°). This column showed, in addition to the expected acetaldehyde (t_R 32 min.) and ethanol solvent (t_R 70 min.), a trace of CH₃Cl (t_R 20 min.) and three unidentified compounds with retention times of 88, 110, and 140 min. No other peaks were detectable, even when the column temperature was raised to 170° and the chromatogram allowed to run for another hour. This eliminates, as detectable products, such possibilities as ethylene glycol, ethylene chlorohydrin, methylaminoethanol, and dimethylaminoethanol. In order to identify the observed peaks, several 0.5 g. crystalline choline chloride samples were irradiated (30 megarads). The volatile products from these samples were pumped into a trap suitable for injection and separated by chromatography on the same "UCON Polar" column, as above. Samples processed in this manner contained only two of the unknown compounds, and it was necessary to process a sample using ethanol as a solvent to obtain the third. Following purification by gas chromatography, the mass spectrum of each of the unknown compounds was determined on a Consolidated Electrodynamics Corporation Model 21-130 mass spectrometer. Comparison

of these spectra with published spectra and spectra of known compounds obtained on our instrument enabled us to identify the first unknown compound (t_R 88 min., appearing only when ethanol was used as a solvent) as the addition product of ethanol and acetaldehyde, acetal. The other two unknown compounds were also products of acetaldehyde, crotonaldehyde (t_R 110 min.), and paraldehyde (t_R 140 min.).

Since the pressure of H_2 in a known volume was read, the quantity could be directly calculated. The quantity of the other components was determined by comparison of their gas chromatographic peak areas with the peak areas obtained when known quantities were chromatographed.

Methyl Chloride as a Radiolysis Product. During the course of earlier work on the radiolysis of choline chloride, traces of methyl chloride had been observed (but not reported) on gas chromatograms used to purify deuterated acetaldehyde and trimethylamine products.³ In the present study, at a total dose of 30 Mrads, only barely detectable amounts of methyl chloride were formed. In the earlier work, higher total doses at higher dose rates were usually employed. Suspecting that either or both of these factors could be responsible for the production of methyl chloride, we prepared four 0.5 g. samples of crystalline choline chloride. Sample one received 30 Mrads at 11.6×10^5 rads/hr. (the same dose rate, and approximately the same total dose as given to all other samples in the present work). Sample two received 30 Mrads at 116×10^5 rads/hr. Sample three received 192 Mrads at 116×10^5 rads/hr. (the dose rate and total dose used in the previous work³). Sample four received 192 Mrads at 11.6×10^5 rads hr. The volatile products from all samples were chromatographed on "UCON Polar", as previously described. Only samples three and four, those receiving

(3) R. M. Lemmon and M. A. Smith, J. Am. Chem. Soc., 85, 1395 (1963).

a total dose of 192 Mrads, contained a detectable amount (about 0.2% of the decomposed choline) of methyl chloride.

Determination of Trimethylamine and Polymer. Current and past work have shown that the trimethylamine produced in the radiolysis appears as the hydrochloride salt. No detectable amounts of trimethylamine had ever been observed until base was added to an irradiated sample. Past work had also indicated that no other amines were being formed in appreciable quantity since radioautographs of paper chromatograms of irradiated methyl-¹⁴C-labeled choline chloride revealed only two active spots; one was undecomposed choline chloride and the other was trimethylamine hydrochloride. In order to confirm this observation by gas chromatography, a 1-g. sample of irradiated choline chloride was transferred to a tube fitted with a side arm bearing a serum cap. The tube was connected to a vacuum line containing a trap suitable for direct injection into the A-350 chromatograph. The system was thoroughly evacuated. Then, sufficient alcoholic KOH to dissolve the sample was added by syringe through the serum cap. The evolved gas and a small amount of the methanol solvent were transferred to the trap and chromatographed on a 10-ft., 0.25-in. column of 15% THFED 5% TEP on 60/80 Chromosorb W (temp. 65°, He F 40 cc./min.) --a column that will cleanly separate NH₃, methylamine, dimethylamine, and trimethylamine. Only trimethylamine (t_R 2.7 min.) was observed on this chromatogram.

Paper (rather than gas) chromatography was chosen as the means of determining the amount of trimethylamine formed, because the amount of undecomposed choline chloride and the amount of polymer formed

could be determined simultaneously. Consequently, two 100 mg. samples of the methyl- ^{14}C -labeled compound, containing a total activity of 9.2×10^4 dpm, were prepared and irradiated (30 Mrads). The samples were stored 422 days, then the tube was opened and the crystals dissolved in 1 ml. of methanol. An aliquot (10 $\mu\text{l.}$) was withdrawn from each sample and chromatographed (one direction) on Whatman No. 1 paper using n-butanol:water:12 N HCl (4:1:1) as a developing solvent. Radioautographs of these chromatograms were used to locate the radioactive spots so that the amount of activity could be measured by a Geiger tube. Trimethylamine hydrochloride and undecomposed choline chloride were the only detectable radioactive spots. Polymeric material, which had been observed previously on the origin of chromatograms from samples given 192 Mrads, was not produced in detectable amounts by the 30 Mrad dose given these samples (under conditions when as little as 1% could have been observed). The percentages of trimethylamine hydrochloride are essentially equivalent to the percentages of choline decomposed.

Search for Cl_2 as a Possible Radiolysis Product. The search for Cl_2 was made by chromatographing all the volatile products from the irradiated crystals; the crystals were dissolved in absolute ethanol and the volatiles (including EtOH) vacuum-line transferred into a trap from which they could be directly injected into a gas chromatograph (Varian Aerograph Model A-350, 5-ft., 0.25-in. column of "Poropak Q", (temp. 50° , He flow rate 40 cc./min.). Under these conditions the t_R for Cl_2 is 2.3 min.

Results and Discussion

The quantitative data on the radiolysis products are presented in Table I and may be summarized as follows:

(1) Experiments 1-3 show that H_2 and CH_4 are only very minor products at doses of about 30 Mrads and post-irradiation storage times of 15 to 232 days. The average percent of decomposed choline appearing as H_2 is 2.7%. This corresponds to a $G(H_2)$ from choline chloride of 1.1. The corresponding average figure for $G(CH_4)$ is 0.9. These are representative G values for the production of H_2 and CH_4 from, for example, saturated hydrocarbons.⁵ Since the radiolysis of crystalline choline chloride has been observed with $G(-M)$ values as high as 55,000,⁴ it is reasonable to conclude that the H_2 and CH_4 come from ordinary, random, radiolytic processes that are unrelated to the unique, chain-decomposition mechanism.

(2) Experiments 4 and 5 demonstrate that CH_3Cl is also a very minor product. We were unable to detect this compound in 30 Mrad irradiations. At 192 Mrads we did find detectable CH_3Cl --about 0.2 percent of the total decomposition products, and independent of the dose rate. The corresponding $G(CH_3Cl)$ is 0.06.

(3) Experiments 6 and 7 show that there is very little polymer formed at 30 Mrads. We know from previous unpublished observations that extensive radiation decomposition leads to more polymer; here, however, at about 30% decomposition, the polymer formation is negligible. What this polymer may be is suggested by the appearance

(5) A. J. Swallow, "Radiation Chemistry of Organic Compounds," Pergamon Press, New York, N. Y., 1960, pp. 61-75.

Table I. Products Appearing in the γ -Radiolysis of Crystalline Choline Chloride

Expt. No.	Dose, Mrads (at 11.6×10^5 rads/hr.)	Time of storage at 25°, days ^a	mmoles choline decomposed	Product formation		
				cpd.	mmoles	% decomp. choline
1	37.2	143	0.372 ^b	H ₂ CH ₄ CH ₃ CHO	0.014 0.008 0.351 ^d	3.8 2.1 94.4
2	34.9	232	0.358 ^c	H ₂	0.008	2.2
3	28.2	15	0.311 ^b	H ₂ CH ₄ CH ₃ CHO	0.007 0.008 0.296 ^e	2.3 2.6 95.2
4	192	1	0.88 ^g	CH ₃ Cl	0.002 ^h	0.2
5	192 ^f	1	1.79 ^g	CH ₃ Cl	0.004 ^h	0.2
6	32.6	422	0.284 ⁱ	(CH ₃) ₃ N polymer	0.288 <0.002	100 <1
7	29.3	15	0.252 ⁱ	CH ₃ CHO (CH ₃) ₃ N polymer	0.242 ^j 0.252 <0.002	96.5 100 <1
8	28.2	181	0.311	Cl ₂	<0.003	<1

^aBetween irradiation and analysis. Earlier work⁴ has shown that, for a given radiation dose, the percent decomp. is dependent upon this time.

^bSum of products found on gas-liquid chromatograms.

^cEstimated from decompositions measured in similar samples.

^dSum of (in mmoles): CH₃CHO (0.022), acetal (0.133), crotonaldehyde (0.023; equiv. to 0.046 CH₃CHO), paraldehyde (0.050; equiv. to 0.150 CH₃CHO).

^eSum of (in mmoles): CH₃CHO (0.011), acetal (0.076), crotonaldehyde (0.004; equiv. to 0.008 CH₃CHO), paraldehyde (0.067; equiv. to 0.201 CH₃CHO).

^fDose rate 116×10^5 rads/hr.

^gBased on amt. CH₃CHO observed from the irradiation of 500 mg. (3.53 mmoles) of choline chloride.

^hAt lower total doses there was no detectable CH₃Cl.

ⁱDetermined by counting undecomposed choline-¹⁴C on paper chromatogram.

^jSum of (in mmoles): CH₃CHO (0.004), acetal (0.091), crotonaldehyde (0.003; equiv. to 0.006 CH₃CHO), paraldehyde 0.047; equiv. to 0.141 CH₃CHO).

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

of crotonaldehyde and paraldehyde (see footnotes d, e, and j). It is well known that aldehydes tend to polymerize on irradiation.⁶

(4) Experiment 7 relates the appearance of acetaldehyde (determined by gas chromatography) to that of trimethylamine (determined by paper chromatography). An exact duplicate of this experiment was performed and led to almost identical results; that experiment, in the interests of space saving, is not recorded in the table. This work further indicates that acetaldehyde and trimethylamine account for nearly all the choline's radiation decomposition. The 96.5% value for acetaldehyde (last column) is a minimal figure; small mechanical losses are expected during transfer operations.

(5) Experiment 8 was a direct search for molecular chlorine as a possible radiolysis product. (Again, a separate experiment, with very similar results, was performed.) This search was made because of the possibility that Cl atoms could be involved in the radiolysis mechanism. If so, one might expect a significant yield of their dimer, molecular chlorine. However, the results of this work indicate that if any Cl₂ is formed it is less than 1% of the decomposed choline (we are unable to set a smaller upper limit because water and Cl₂ have the same retention time on our "Poropak" columns).

The present work clearly indicates that the decomposition mechanism is very clean. The chain mechanism leads very specifically to a scission of the choline cation between the nitrogen atom and the adjacent methylene carbon, leading to the production of trimethylamine and acetaldehyde. For doses up to about 3×10^7 rads, and approximately

(6) J. C. McLennan and W. L. Patrick, Can. J. Res., 5, 470 (1931).

30% choline decomposition, all other products comprise, at most, only 3% of the total radiolysis yield.

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