RADIATION MEASUREMENTS: COMPARISON OF RADIOLYSIS EFFECTS OF COBALT-60 GAMMA RAYS AND 3-6 MEV ELECTRONS ON NITRILE SYSTEMS

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INTRODUCTION

In the conduct of any radiation chemistry study, it is imperative that the amount of radiation absorbed by the system be precisely known . Chemical dosimeters, which absorb energy in a manner closely approaching that of the system, are preferred over ionization chambers or other devices. The most widely used chemical dosimeter is the Fricke ferrous-sulfate dosimeter, but it is limited to a maximum dose of about 50,000 rads. For the powerful radioactive gamma-ray sources now available, for nuclear reactors, and for high-intensity accelerators, a chemical dosimeter of much higher dose range is required. A really useful dosimeter in the range of 10^6 through 10^8 rads is necessary for many phases of radiation work and is of particular advantage when an integrated dose, rather than an instantaneous dose rate, is needed for radiation sources with time-variable intensities.

Much study of radiation measurements has been made, [1-5] but no fully satisfactory chemical dosimeter has been developed for the high ranges.[6] Ceric sulfate, although sensitive to impurities and formerly useful only in the 10^6 to 10^7 range, has recently been extended to 1.4×10^8 rads, but this appears to be about the limit because of solubility problems.[7] Nitriles, especially acetronitrile, were chosen as systems for evaluation. They are normally quite stable, can be easily purified, have low cross section for neutron activation, and should give CN compounds on radiolysis which can be detected in low concentration.

The study of nitriles affords the opportunity to examine the radiolysis products and gain some understanding of the mechanism involved. Also, it enables determination of whether radiation from an accelerated electron beam differs in its action from cobalt-60 gamma-radiation. Energy dependence would probably not be a

factor,[8-12] but the high instantaneous dose rate from the linear accelerator, which was approximately one-half million times that from the isotope source, might conceivably alter the reaction yield G value (molecules affected per 100 electron volts of energy absorbed). The most direct way to measure the absorbed dose from the beam would be to determine calorimetrically the heat developed per unit mass at the location of interest, but Whyte[13] indicated that this as yet had not proved experimentally feasible.

EXPERIMENTAL PROCEDURE

Equipment

The cobalt-60 source had a nominal 29,100 curies, and irradiation dose rates were generally from 0.4 to 0.7 megarads per hr. The linear accelerator was an Applied Radiation Corporation Model 1-F4. It was operated at 1.2 to 2.1 kilowatts, with a beam current of 457 to 560 microamperes, 360 pulses per sec., maximum electron energy of 6 mev, and average energy of 3.5 to 4 mev. At 10 microsecond pulse length, the instantaneous dose rate was approximately 6.7×10^7 rads per sec., or 484,000 times that from the isotope source.

Analytical Methods

Radiolysis product identities and yields were determined by a combination of infra-red, low and high mass, and nuclear magnetic-resonance spectroscopy, by gas chromatography, and by CN analysis. The latter, which was the test used for dosimetry, was done by the method of Schilt.[14] This is a colorimetric determination in which ferroin * forms a violet-colored complex with CN after suitably buffering and heating the sample and reagent in a boiling water bath for exactly 15 min. The CN content is based on calibration curves, prepared by using standard KCN solutions.

Calorimeter

Calorimeters were built so that the contained liquid absorbed all of a collimated ½ in. diameter electron beam. The energy absorbed was measured as temperature rise of the calorimeter liquid. Corrections were made for energy absorbed in the 3.5 mil. thick aluminum window (1.5 per cent) and for the heat of reaction of the

*Ferroin is tris (1, 10-phenanthroline) — iron (II) ion.

radiolysis products (2.5 per cent). The concurrent chemical change of the liquid, matched against the energy absorption, gave the absolute measure of the radiation G value. Heat loss from the calorimeter was minimized and kept constant and reproducible. Calibration was done by measuring temperature rise data when adding known amounts of electrical energy to resistance coils in the calorimeter. Calculations of energy absorbed were based on the product of weight (W) and specific heat (C_p) of the acetonitrile, and the adjusted temperature rise (ΔT). The latter was determined by the method of White.[15,16] The same procedure for both calibrations and actual runs eliminated the need to measure heat loss.

The calorimeter vessel attached to the collimator and bottom end of the linear accelerator is shown in FIGURE 1 and the complete assembly is shown in FIGURE 2.
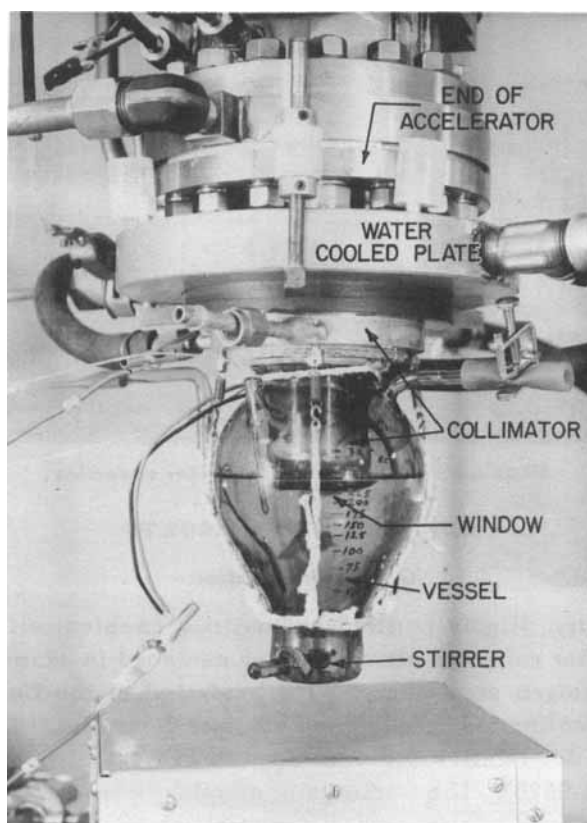

FIGURE 1. Calorimeter vessel attached to collimator and linear accelerator.
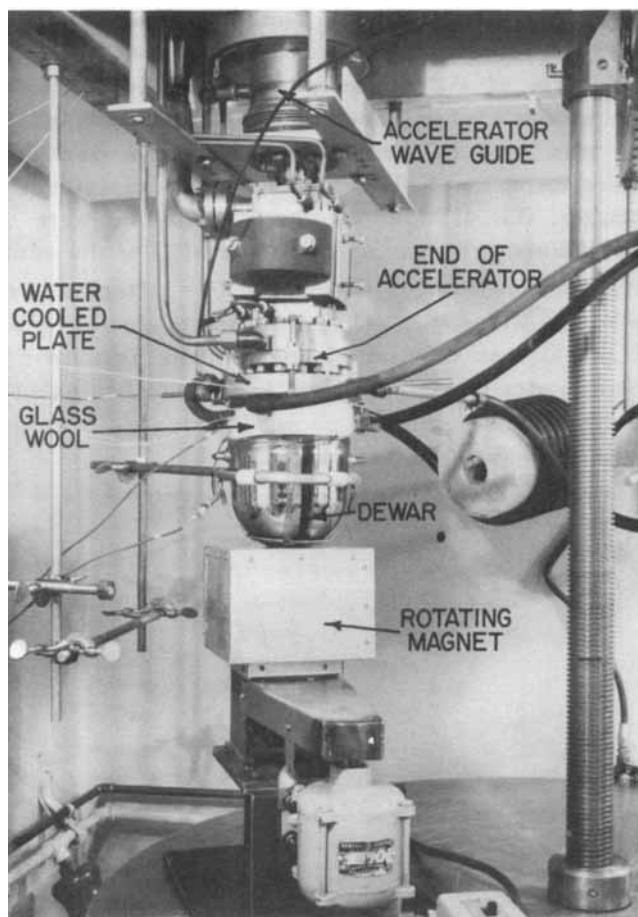
FIGURE 2. Complete calorimeter assembly.

EXPERIMENTAL RESULTS

Gamma-Irradiation

Dosimetry. Highly purified acetonitrile samples, either sealed in tubes after complete air removal or enclosed in screw-top vials under a nitrogen atmosphere, were irradiated in the Co-60 source previously calibrated by the ferrous sulfate dosimeter.[17] Corrections were made for relative electron density of acetonitrile to sulfate solution (0.9686). The radiolysis reaction was measured by CN analysis and examination of differential infra-red spectra. It was observed that the CN yield was not due to free HCN, as initially expected, but rather to a nonvolatile component or polymer.

Variables. The effects of a number of variables were determined. The results of the addition of water, oxygen, and metals are shown in FIGURE 3, TABLE 1, and TABLE 2, respectively. Water causes an increasing and then decreasing yield of CN and should be completely absent from the dosimeter liquid. Although air does not appear to have a major effect, oxygen increases the apparent CN yield, reduces a characteristic infra-red absorption peak at 4.58 microns and gives indication of carbonyl material being formed.
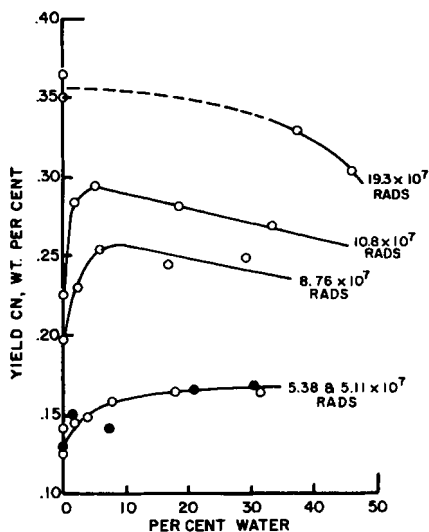

FIGURE 3. Effect of water on radiolysis of acetonitrile.

Both oxygen and air should be excluded during irradiation. The metals of TABLE 2 had no apparent catalytic effect as judged by CN and infrared analysis, and therefore, should be permissible in radiation tubes or calorimeter equipment. Copper, however, was very badly attacked by the nitrile during irradiation (possibly due to NH_3 or amine products) and cannot be used. A series of runs at temperatures from 75° F. to 140° F. showed no thermal influence, as indicated by the following tabulation:

Temperature, ° F.	Relative CN yield per equivalent dose
75	6.67
100	6.56
120	6.38
140	6.44
Average	6.51

TABLE 1

EFFECT OF OXYGEN ON RADIOLYSIS OF ACETONITRILE

Oxygen	Dose rads $\times 10^7$	CN yield wt. per cent	Infra-red absorption at $4.58\,\mu$
None	5.20	0.11	
Air saturated	5.20	0.11	
Air saturated	5.20	0.12	
None	7.61	0.167	0.258
O_2 saturated	7.61	0.211	0.228, Carbonyl
None	15.94	0.305	
O_2 saturated	15.94	0.321	
N_2 saturated	5.38	0.133	0.145 Trace carbonyl
O_2 saturated	5.38	0.150	0.135 Carbonyl

However, irradiation of a sealed sample at the boiling point (180° F.) produced visible polymer which came out of solution. The phase separation made sampling difficult and relative values varied from 9.38 to 11.7. Boiling alone gave a zero CN yield.

TABLE 2

EFFECT OF METALS ON RADIOLYSIS OF ACETONITRILE

Metal	CN yield wt. per cent	Infra-red absorbences*		
		$2.98\,\mu$	$4.58\,\mu$	$6.08\,\mu$
None	0.410	0.080	0.056	0.163
None	0.394	0.082	0.058	0.164
Platinum	0.399	0.080	0.058	0.162
Chromel A	0.408			
Nickel	0.402			
Nichrome	0.404			
Aluminum	0.418	0.080	0.058	0.162
Average value	0.405			
Standard deviation from average	0.0248			

Dose, 14.4×10^7 rads; sealed in tube.
* 50-micron cell, no multiplication. These peaks are formed proportional to radiation dose.

Data in a similar vein showed no effect for exposure of aceto-
nitrile to ultraviolet light either before or after gamma-irradiation.
However, for good handling technique, excessive exposure to bright
sunlight should be avoided.

Dosimeter Correlation — Dose versus CN Yield for Acetonitrile

The relationship between the yield of CN and the dose appears
to be linear over short ranges, but when plotted over several dec-
ades, the yield tends to fall off slowly. A plot of the logarithm of
CN yield as weight per cent *versus* the logarithm of dose in mega-
rads gives a straight line over the entire extent of the data. This
is seen in FIGURE 4. In order to establish the line with precision.

EQUATION OF LINE
CN = .0050 (DOSE)$^{.8245}$
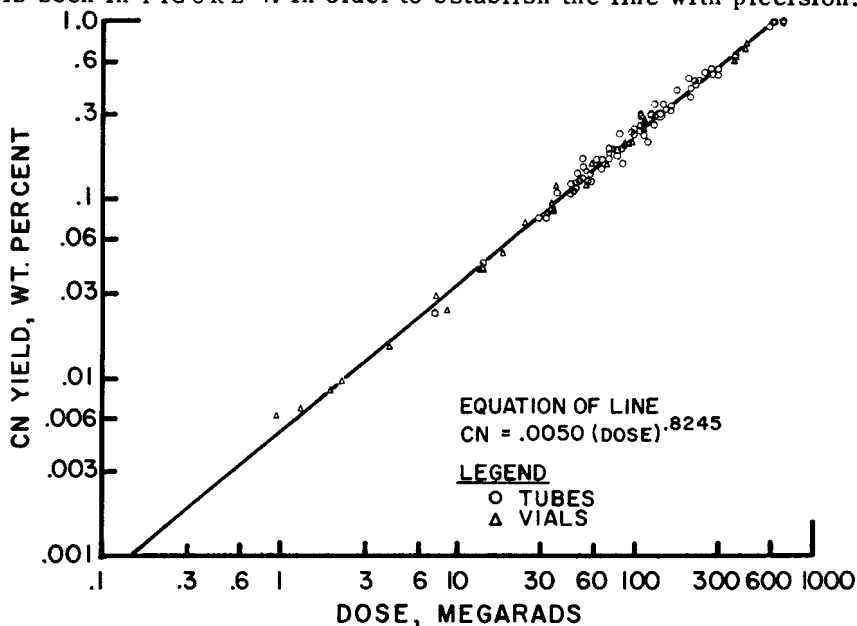
LEGEND
O TUBES
△ VIALS

FIGURE 4.   Radiolysis of acetonitrile. Yield of CN as a function of
dose. Irradiation in tubes and vials.

the data were processed on the IBM 650 computer using a standard
step-wise regression program.[18] The computation showed that the
logarithmic equation of the straight line is: ln CN = −5.298
+0.8245 ln dose. This can be converted to the form $Y = a(X)^b$ or:
CN = 0.0050 (Dose)$^{0.8245}$ The program indicated a high degree of
correlation fit and showed that the log-log relationship was real.
The individual values of CN yield were calculated from the equa-
tion and compared to the experimental CN values. The difference

between the two, divided by the calculated values and multiplied by 100, gave, in a sense, the per cent by which the experimental CN values differed from the correlation fit. The average difference was 6.02 per cent with a standard deviation of 7.78.

Detailed data are not shown here, but it was found that irradiation in the atmosphere, rather than below water in the isotope storage well, and use of sealed tubes, rather than nitrogen-blanketed screw-capped vials, permitted improved precision.

Calorimeter Runs on the Linear Accelerator

Calibration. As previously described, the calorimeters were calibrated under conditions simulating actual runs as closely as possible. A summary of efficiencies based on linear ΛT adjustment is shown in TABLE 3.

TABLE 3

SUMMARY OF CALIBRATION EFFICIENCIES - LINEAR ADJUSTMENT

	Efficiency per cent	Difference from average	Per cent difference
Calorimeter no. 1	85.66	−0.68	−0.79
	86.95	+0.61	+0.71
	86.76	+0.42	+0.49
	85.47	−0.87	−1.01
	86.88	+0.54	+0.62
Average	86.34	Std. error 0.718	
Calorimeter no. 3	83.76	+0.61	+0.73
	83.66	+0.51	+0.61
	82.52	−0.63	−0.76
	83.43	+0.28	+0.34
	83.12	−0.03	−0.04
	82.40	+0.03	+0.04
Average	83.15	Std. error 0.528	

Calorimeter runs. The accelerator was adjusted to give the desired beam, and when operation was stabilized it was turned off so that the filled calorimeter could be attached and thermocouples connected. The machine was again turned on and quickly readjusted to operating conditions, and thereafter, held constant. After shutdown, temperature measurements were continued for about 15 min. to get an adequate cooling curve. Calculations of dose were made by using both linear and semi-log plot adjustments of ΔT. Results by each method were close, as was expected, and the values were averaged. Typical data for the linear adjustment are shown in TABLE 4, along with a summary of semi-log and average doses.

Analytical Results, Calorimeter Runs, and Correlative Co-60 Runs

The electron irradiated calorimeter products were analyzed for gas, liquid, polymer, and CN yields. Two runs were also made with the calorimeters arranged in the center of the cobalt-60 source array and irradiated to a dose of 1.04×10^7 rads. Products were analyzed in the same manner as the accelerator runs. The radiolysis of a limited number of sealed radiation tubes of acetonitrile were also made on the cobalt source at dosages comparable to the calorimeter runs. This was done so that analyses of samples from the tubes could be interspersed with those of the calorimeters to minimize the effect of possible systematic errors. The CN yields and G values are shown in TABLE 5, and the CN data are plotted in FIGURE 5. It may be seen that the internal agreement of the group is quite good. Because of the nonlinear relationship between CN yield and dose, the G values also vary with dose. However, over a narrow range, the G values should be relatively constant, and therefore, those for the calorimeter runs have been averaged ($G_{CN} = 1.42$) and compared to the average of the correlative cobalt-60 data ($G_{CN} = 1.38$) over the same narrow dose range (6-15 megarads). This uncorrected difference is 2.85 per cent. However, as the subsequent sections show, the required correction to the calorimeter is a four per cent reduction in dose. This increases the G_{CN} value to 1.48 and represents a possible difference from cobalt-60 of 7.0 per cent. This is not considered significant.

The above indicates an absence of dose-rate dependence up to the 6.7×10^7 rads per sec. used here and is consistent with the results of Sutton and Rottblat.[19, 20] They found with a 15 mev accelerator that there was no change in G value for ferrous sulfate below 7.6×10^7 rads/ sec., although it did decrease at higher rates.

TABLE 4

CALORIMETRIC DATA - LINEAR ACCELERATOR RUNS WITH ACETONITRILE

Calorimeter	1	1	1	1	3	3
Run number	7	9	11	13	A	B
Temperature in calorimeter						
Start, mv.	1.25	1.135	1.04	1.47	1.32	1.04
Max. mv.	2.59	3.68	3.58	3.605	3.22	3.00
Mean temp. mv.	1.92	2.408	2.31	2.538	2.27	2.02
°C.	37.4	46.6	44.4	49.1	44.1	39.3
Linear adjustment						
Start, °C.	24.9	22.7	21.7	29.0	26.35	22.1
Max., °C.	52.4	74.7	73.5	74.8	65.5	64.6
ΔT, temp. rise, °C.	27.5	52.0	51.8	45.8	39.15	42.5
Adjusted specific heat	0.5515	0.5635	0.5585	0.5605	0.5585	0.556
Wt. acetonitrile, gm.	212.28	211.85	194.19	205.23	233.74	242.64
$W\, C_p\, \Delta T$, calories	3219	6208	5618	5268	5111	5733
Watt-hr.	3.734	7.201	6.517	6.111	5.929	6.650
Time of run, min.	16.4	8.8	11.8	13.0	11.5	23.3
Apparent watts	13.66	49.09	33.1	28.20	30.93	17.12
Calorimeter efficiency, %	86.34	86.34	86.34	86.34	83.15	83.15
Corrected calories	3728	7190	6507	6101	6147	6895
Cergs (100 ergs) $\times 10^6$	15.58	30.05	27.20	25.50	25.69	28.82
Rads, 100 ergs/gm. $\times 10^7$	0.734	1.42	1.40	1.24	1.10	1.19
Semi-log adjustment						
Rads, 100 ergs/gm. $\times 10^7$	0.743	1.46	1.39	1.25	1.10	1.16
Average dose, rads $\times 10^7$	0.739	1.44	1.40	1.25	1.10	1.18

TABLE 5

COMPARISON OF LINEAR ACCELERATOR AND COBALT-60
RADIOLYSIS YIELDS OF CN

Calorimeter results				
Accelerator run no.	Product degassed	CN yield wt. %	Dose rads × 10⁶	G_{CN}
7	Yes	0.0285	7.39	1.43
9	Yes	0.053	14.4	1.37
11	Yes	0.049	14.0	1.30
13	Yes	0.051	12.5	1.51
A	Yes	0.044	11.0	1.48
B	Yes	0.045	11.8	1.42

Cobalt-60 results				
Vessel no.	Product degassed	CN yield wt. %	Dose rads × 10⁶	G_{CN}
Cal. 1	Yes	0.0355	10.4	1.27
3	Yes	0.0365	10.4	1.30
Tube 25	Yes	0.023	6.0	1.42
26	No	0.026	6.0	1.61..
27	Yes	0.033	9.0	1.36
28	No	0.036	9.0	1.48
35	Yes	0.039	11.0	1.32
36	No	0.043	11.0	1.45
70	Yes	0.045	13.0	1.28
71	No	0.047	13.0	1.34
34	No	0.053	15.0	1.31
72	No	0.004	0.93	1.60
52	No	0.007	1.86	1.40
310	No	0.015	3.71	1.50

Correction to Calorimeter Data

Heat of reaction. A correction would have to be made for any heat given up by the acetonitrile in forming its products. Because of low G values, the heat evolved, compared to that absorbed from the beam, was expected to be low. This was also true since many of the "cracking" reactions were endothermic and would counter-balance the exothermic "polymerization" reactions. The over-all heat of reaction was calculated on the basis of the yield of each component (TABLE 6) and the known heat of combustion of each
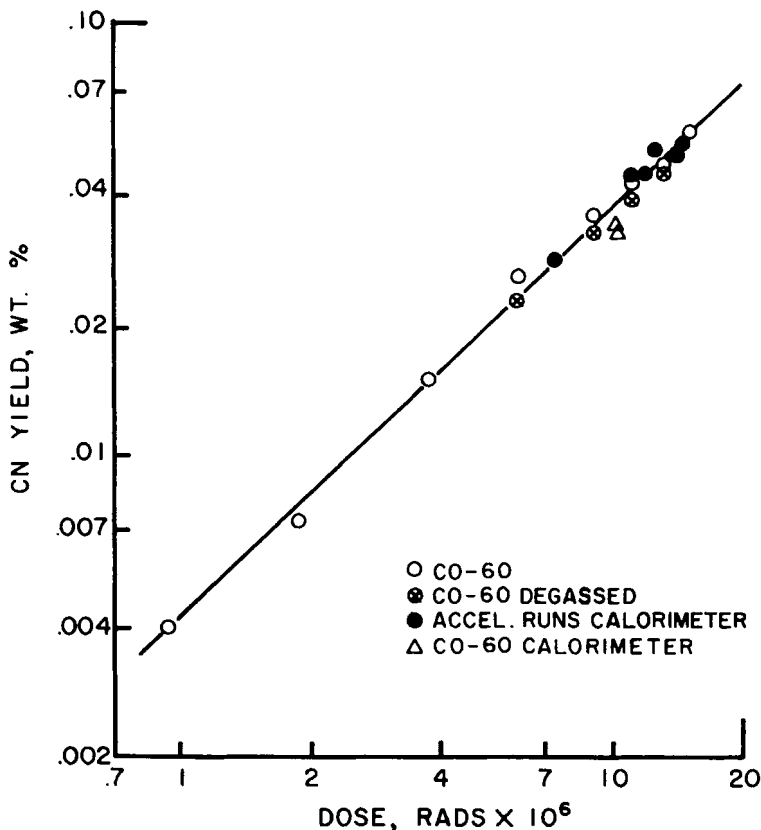
FIGURE 5. Accelerator runs and correlative Co-60 data. CN yield *vs*. dose.

product. This was true for all except the acetonitrile polymer, whose value was experimentally found to be 7063 calories per gm. in comparison to 7467 for acetonitrile. The over-all heat of reaction was determined to be 168 calories per gm. Considering the fraction of acetonitrile present which reacted (related to $G_{CH_3CN} = 8.55$), this represents a 2.54 per cent correction.

Energy absorbed by calorimeter window. The thin aluminum window of the calorimeter would be expected to have a minimal effect on the beam. Electrons converted to bremsstrahlung X-rays would bring about chemical change in the liquid and would already be accounted for in the calorimeter measurements, but the beam energy absorbed in the window and converted to thermal energy could heat the contacting liquid without a corresponding radiolysis change. Graphical integration of data of Trump, Wright, and Clarke[21]

TABLE 6

SUMMARY OF ACETONITRILE RADIOLYSIS PRODUCTS OBTAINED

Compound	G Value	Per cent of gas	Classification	Method of analysis*
Gases				
Hydrogen	0.578	42.8	Major	M.S.
Methane	0.626	46.4	Major	M.S.
Ammonia	0.051	3.8	Minor	M.S.
Ethane	0.031	2.3	Minor	M.S.
Acetylene	0.024	1.8	Minor	M.S.
Nitrogen	0.019	1.4	Minor	M.S.
Hydrogen cyanide	0.012	0.9	Minor	M.S.
Propane	0.004	0.3	Minor	M.S.
Butane	0.004	0.3	Minor	M.S.
Trace Gases				
Ethylene			Trace	M.S.
Propylene			Trace	M.S.
Butylene			Trace	M.S.
Methyl acetylene			Trace	M.S.
Ethyl acetylene			Trace	M.S.
Liquids				
Propionitrile	0.235		Major	G.C.
Butyronitrile			Trace	G.C.
Valeronitrile			Slight trace	G.C.
Solids				
Total polymer (as CH₃CN)	7.99		Major	wt.
Acetonitrile dimer			Major	IR,NMR,HMS
Succinonitrile	0.17		Major	IR,NMR,GC
Malononitrile			Trace	GC
Acetonitrile trimer			Trace	IR
Acetonitrile tetramer			Trace	IR
Acetonitrile disappearance	8.55			

*M.S., Mass Spectrometer; HMS, High-Mass Spectrometer; G.C., Gas Chromatography; IR, Infra-red; NMR, Nuclear Magnetic Resonance; wt., Weight

shows that the 0.009 cm. window could absorb 2.09 per cent of the beam at 2 mev, and 1.29 per cent at 3 mev. At the 3.5 to 4 average mev energy of the accelerator beam, the absorbency would be expected to be less than one per cent. However, the data from Trump *et al.*, were for monoenergetic electrons, and the proportion of low-energy electrons in the present beam is not currently known. To be conservative, 1.5 per cent absorption was assumed.

TABLE 7

SUMMARY OF POLYMER ANALYSIS -
COMPARISON OF CALORIMETER AND CORRELATIVE COBALT-60 RUN
DATA AT LOW DOSE WITH COBALT-60 RESULTS AT HIGH DOSE

	Low-dose calorimeter and Correlative Co-60 runs		High-dose Cobalt-60 data	
	Range of values	Average values	Range of values	Average values
Dose, rads $\times 10^7$	0.74 - 1.44	1.16	15.7 - 79.2	52.4
Polymer yield	0.244 - 0.455	0.388		
CN yield basis polymer basis acetonitrile	4.3 - 8.0 0.0165 - 0.035	5.8 0.023		
$G_{polymer}$	6.81 - 9.52	7.99	5.71 - 8.52	6.3
G_{CN}	0.49 - 0.996	0.735	0.306 - 0.446	0.38
Molecular weight	135 - 143	138	206 - 237	223

Gas Yields

The radiolysis gases removed from radiation tubes and calor-
imeters were analyzed by mass spectrometer. The yields expressed
as G values are shown in TABLE 6, along with some liquid and
polymer yields. Hydrogen results from both gamma- and electron-
irradiation were statistically equivalent. Other products, ex-
cept for methane, checked closely, and the values are the average
from both types of irradiation. The methane value from the accel-
erator was 0.316 and is statistically different from 0.626 from
gamma irradiation.

Acetonitrile Polymer

The yield of polymer appears to be linear with dose, as shown
in FIGURE 6. Elemental analyses show an average of C = 58.28,
H = 6.26, N = 35.51. This is quite close to $(CH_3CN)_x$, which is
58.51, 7.37, and 34.12 for the three elements. TABLE 7 compares
values for low-dose versus high-dose polymers. The $G_{polymer}$
values of 7.99 and 6.3 respectively, are not believed significantly
different in view of FIGURE 6 and the overlap in values. How-
ever, the difference in G_{CN} yield at the two levels is believed to
be real, and G_{CN} can be shown to decrease as a function of dose,
as it does in the case of the total liquid analysis. The molecular
weight data are insufficient to establish an ordered function of
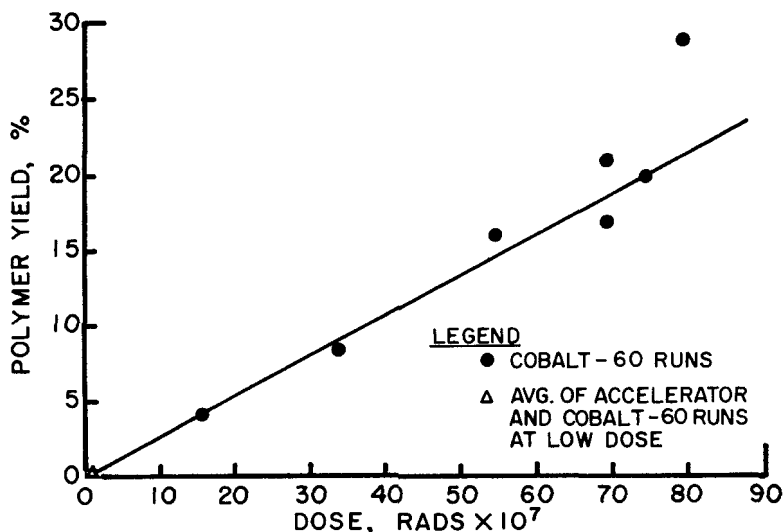dose, but they both increase together.

FIGURE 6. Yield of acetonitrile polymer as a function of dose.

High mass spectrometer data, taken at low voltage (8V) to minimize fragmentation, are given in FIGURE 7. The results show that the polymer is not a limited number of specific compounds, but is a wide assortment of molecules having a range of molecular weights. It is strikingly apparent, however, that the three spectra from widely varying doses all show maximum component concentrations at the same mass numbers. This is strong evidence of an ordered reaction. The large peak at 82 was the dimer, 3-imino-butyronitrile.
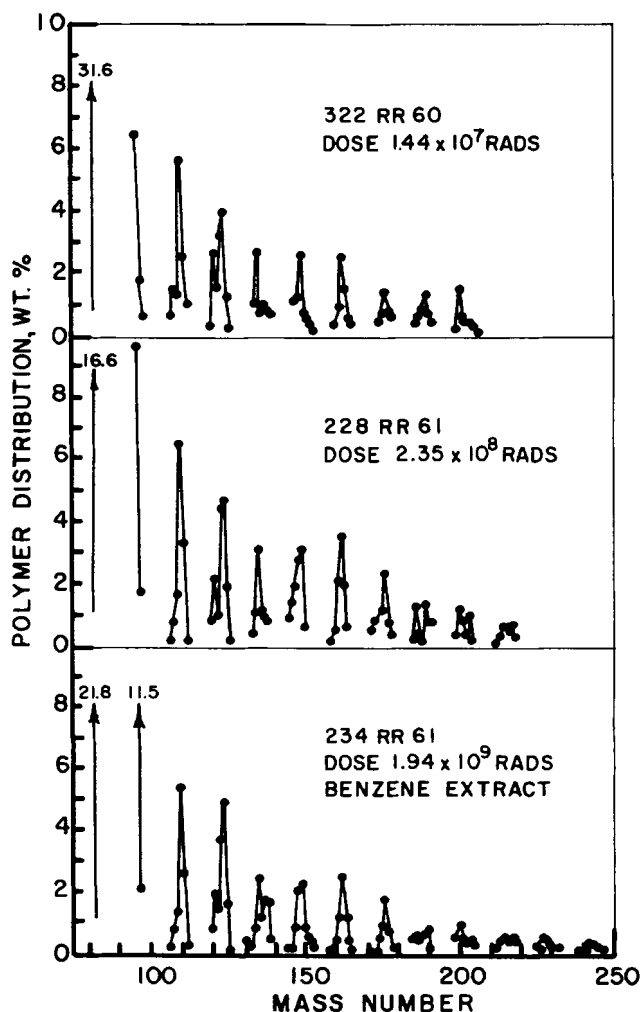
FIGURE 7. Polymer distribution as a function of molecular weight; high-mass spectrometer data at 8 volts.

Infra-red Analyses of Irradiated Nitrile

Infrared was used to determine the effect of dose on spectra of irradiated nitrile and to obtain clues to the polymer structure. The spectra were complex, but peaks at 2.98, 4.58, and 6.08 microns were observed to grow with dose as shown in FIGURE 8.
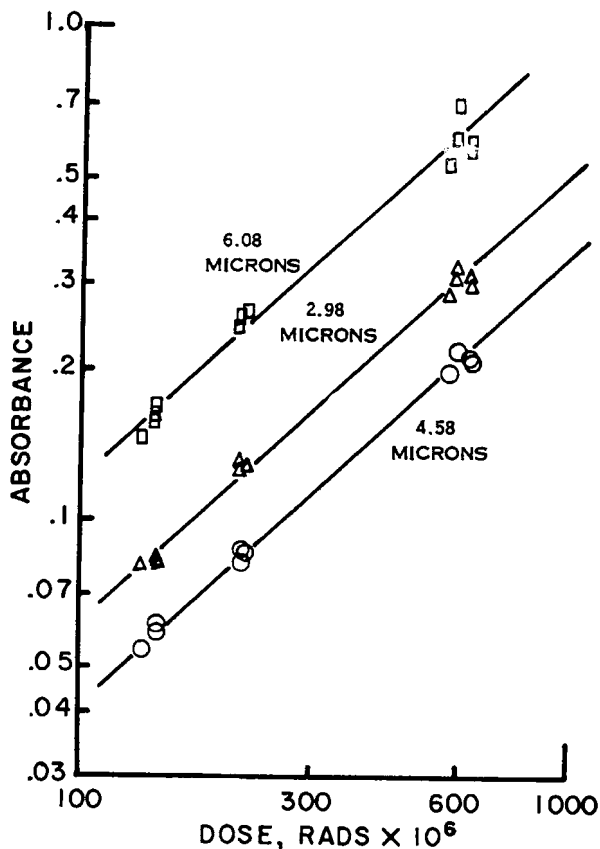

FIGURE 8. Infra-red absorbence as a function of dose; 50-micron cell, no multiplication.

These log-log curves cover the higher doses (10^8 rad range), and the parallelism for the three peaks indicates the structural character of the polymer does not change over wide ranges of dose. Infrared shows some promise as a quick method of analysis for dosimetry in this region. At lower levels, however, the absorbency is less, and it is necessary to use 5X machine multiplication to obtain sufficient peak height. The data scatter becomes large, and the CN analysis is more precise and of wider applicability.
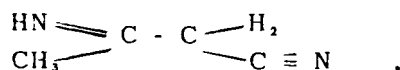
For the three peaks, the 2.98 and 6.08 ones are in regions assigned to imines or amines,[22,23] and the 4.58 peak is close to the doublet $C \equiv N$ peak of acetonitrile at 4.37 and 4.44. A sample of acetonitrile dimer was prepared, and the three peaks in question were typical of the dimer spectrum. Methyl isonitrile, CN_3NC, with a peak at 4.63, could be resolved in a mixture with dimer and was shown not to be present in irradiated samples in more than a trace, if at all. Succinonitrile, $NCCH_2CH_2CN$, with a characteristic nitrile peak at 4.44, and peaks matching the polymer at 9.98, 10.37, and 10.90, was established as being present. Spectra of acetonitrile trimer and tetramer, substituted aminopyrimidines, indicate their possible presence in very low concentration.

Nuclear Magnetic Resonance

Data from *NMR* spectra indicate characteristic peak increases with dose, and their occurrence and distribution are not altered at high dose. The spectra are complex, but $= CH$ groups at 242 and 223 cps, * and amine groups (broad around 300 cps) were observed. These were shown to be due to acetonitrile dimer. Succinonitrile (165 cps) and methane (9 cps) were present, but HCN(263 cps) and CH_3NC (triplet at 190 cps) were undetected. The dimer was shown to have the amine form,

$$
\begin{array}{c}
H_2N \\
CH_3
\end{array}
\!\!\!>\!\! C = C \!<\!\!\!
\begin{array}{c}
H \\
C \equiv N
\end{array}
\quad ,
$$
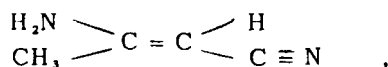
rather than the imine form,

$$
\begin{array}{c}
HN \\
CH_3
\end{array}
\!\!\!=\!\! C - C \!-\!\!\!
\begin{array}{c}
H_2 \\
C \equiv N
\end{array}
\quad ,
$$

and to undergo *cis-trans* isomerization about the $C = C$ bond, possibly explaining the two melting points reported by Von Meyer.[24]

Gas Chromatography

G.C. analysis of irradiated acetonitrile on a column using Quadrol showed peaks identifiable as propionitrile, butyronitrile, and valeronitrile. A column using 10 per cent silicone nitrile XF 1150 on Chromasorb W showed the presence of succinonitrile and malononitrile. The acetonitrile dimer, 3-iminobutyronitrile, known

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*Cycles per second shift from tetramethyl silane reference.

to be present from *IR*, high mass, and *NMR* data was not detected. Either the dimer is too polar or it breaks down under the column conditions (200° C.).

Possible Reaction Mechanism

The radiolysis of many systems has been shown to proceed by the general mechanism of radiation bond splitting, hydrogen abstraction, and random free radical recombination.[25, 26, 27] The formation of most of the identified products shown in T A B L E 6 can be satisfactorily accounted for in this way. Because of the relatively small size of the CH_3CN molecules, there is a limited number of bonds which can be ruptured. The resulting free radicals include $\dot{C}H_2CN$, $\dot{H}$, $\dot{C}H_3$, $\dot{C}N$, $CH_3\dot{C}$, $\dot{N}$, and a postulated * diradical $CH_3\dot{C} = \dot{N}$. Free radical recombination or hydrogen abstraction from the bulk CH_3CN can readily account for H_2, CH_4, NH_3, C_2H_6, N_2, HCN, CH_3CH_2CN, and $NCCH_2CH_2CN$. The dimer appears to be formed by reaction between the diradical and acetonitrile [28] and proposed mechanisms for the other products can be made in a similar manner.

CONCLUSIONS

The following conclusions are made: (a) Purified acetonitrile makes a satisfactory dosimeter over the range examined, 1×10^6 to 6.5×10^8 rads; (b) the weight per cent yield of CN is an exponential function of total dose in megarads, as given by: CN = (0.005) (Dose)$^{0.8245}$; (c) the principal gaseous products are H_2 (G = 0.58) and CH_4 (G = 0.63), with minor yields of NH_3, C_2H_6, C_2H_2, N_2, HCN, C_3H_8, and C_4H_{10}; (d) identified heavier products are C_2, C_3, and C_4 aliphatic nitriles, succinonitrile, malononitrile and acetonitrile dimer (3-iminobutyronitrile); (e) a complex polymer (G = 8) contains imine or amine and nitrile groups, the C-H-N proportions approach $(CH_3CN)_x$, and the measured CN yield used in dosimetry is largely contained in the polymer; (f) a new calorimetric method for absolute dose measurement of the electron beam is satisfactory; and (g) the high instantaneous dose-rate electron beam is not significantly different in its action from gamma-radiation, as judged by hydrogen and CN yield.

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