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CHEMISTRY DIVISION QUARTERLY REPORT

March, April, May 1954
July 8, 1954

Berkeley, California

CHEMISTRY DIVISION QUARTERLY REPORT

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Contents

BIO-ORGANIC CHEMISTRY

Effects of Ionizing Radiation on Choline and its Analogs 4

Photolysis of Trimethylene Disulfide 13

Enzymatic Carboxylation of Ribulose Diphosphate 19

The Effect of Cobalt-60 Irradiation on Respiratory Metabolism in Mice 21

The "Cosmic Ray" Effect in Photomultiplier Tubes 23

Studies on Adenine Metabolism 26

Synthetic Organic Chemistry 31

Irradiation Decomposition of Pure Organic Compounds. 34

Rate Studies in Photosynthesis. 35

Respiratory Metabolism of Labeled Organic Compounds 38

Study of a Reaction Mechanism 41

NUCLEAR CHEMISTRY

Bismuth-207. 44

Neutron-deficient Platinum, Gold,and Mercury Isotopes 45

Further Investigation of the Alpha Spectrum of Emanation-211 46

Emanation Isotopes from Gold 47

Beta Decay of Neptunium-238 51

Neptunium-240. 54

The Alpha Decay of Protactinium-231 55

The Low-Intensity Alpha Groups of Americium-243 57

The Alpha Groups of Californium-246 59

* Previous Quarterly Reports: UCRL-2531, UCRL-2455

The Gamma Radiations and Gamma-Gamma Coincidences in the Decay of Actinium-226 60

Alpha Decay of Spheroidal Nuclei 64

X-Ray Investigation of $CH_3\overset{S}{C}NHNH\overset{S}{C}NH_2$ and KF• x HF 64

Preliminary Investigation of Potassium Hydroxylamine Sulfonates 64

Determination of Structure of Auric Chloride 65

Bent-Crystal X-Ray Spectrometer 65

Double-Retarding-Field Electrostatic Beta-Ray Spectrometer . . 66

Nuclear Quadrupole Resonance 67

Optical Spectroscopy 68

Mass Spectroscopy 68

Gadac 70

Snapper Pulse-Height Analyzer 71

Sealed-Tube Digestion for Organic Analyses 78

CHEMICAL ENGINEERING (PROCESS CHEMISTRY)

Notes on Experiments in Progress 82

GENERAL CHEMISTRY

Metals and High-Temperature Thermodynamics 84

Basic Chemistry, including Metal Chelates 85

CHEMISTRY DIVISION QUARTERLY REPORT

March, April, May 1954

July 8, 1954

BIO-ORGANIC CHEMISTRY

M. Calvin, Director
Edited by B. M. Tolbert

EFFECTS OF IONIZING RADIATION ON CHOLINE AND ITS ANALOGS

Richard M. Lemmon and Margaret A. Parsons

The abnormal sensitivity of choline-methyl-C_1^{14} chloride towards its own radiation (Quarterly Report for February, 1953; J. Am. Chem. Soc. 75, 1867 (1953) has led to the present work of determining the effects of changes in the choline molecule on its radiation sensitivity. Beta (2-4-Mev) and gamma (1.3-Mev) irradiations have been carried out on choline chloride, $[(CH_3)_3NCH_2CH_2OH]^+Cl^-$, and the following choline analogs:

acetylcholine chloride	$[(CH_3)_3NCH_2CH_2OCOCH_3]^+ Cl^-$
choline iodide	$[(CH_3)_3NCH_2CH_2OH]^+ I^-$
trimethylethyl ammonium chloride	$[(CH_3)_3NCH_2CH_3]^+ Cl^-$
trimethyl-2-chloroethyl ammonium chloride	$[(CH_3)_3NCH_2CH_2Cl]^+ Cl^-$
trimethyl-3-hydroxypropyl ammonium chloride	$[(CH_3)_3NCH_2CH_2CH_2OH]^+ Cl^-$
betaine hydrochloride	$[(CH_3)_3NCH_2COOH]^+ Cl^-$

The present report concerns the results of these irradiations.

Experimental Procedure

Preparation of Choline Analogs

With the exception of the betaine hydrochloride, all the compounds used in this work were prepared with carbon-14 in the methyl groups. Choline-methyl-C_1^{14} iodide (sp. act. 0.1 μc/mg) was prepared by reacting $C^{14}H_3I$ with dimethylaminoethanol in methanol solution and recrystallizating the product from absolute ethanol-ether. (All the preparations, with the exceptions of betaine hydrochloride and trimethyl-3-hydroxypropyl ammonium chloride, as noted below, were recrystallized from this solvent.) The chloride was prepared from the iodide through conversion to the quaternary base with Ag_2O, followed by titration with HCl. Acetylcholine chloride was prepared by refluxing the labeled choline chloride with acetic anhydride for 2 to 3 hours. The trimethyl-2-chloroethyl ammonium chloride was prepared by reacting the choline chloride-C^{14} with thionyl chloride at room temperature.

Trimethyl-C_1^{14}-3-hydroxypropyl ammonium chloride (sp. act. 1.0 μc/mg) was prepared (Quarterly Report for February, 1954) from labeled trimethylamine and 3-chloropropanol; the product was recrystallized from absolute ethanol-dioxane. Trimethyl-C_1^{14}-ethyl ammonium chloride (sp. act. 0.1 μc/mg) was prepared by reacting labeled trimethylamine with ethyl iodide, followed by conversion of the quaternary iodide to the chloride.

The betaine hydrochloride used in these studies was not labeled. A recrystallized (from 90% ethanol) commercial product was used.

Acceptable carbon, hydrogen, nitrogen, and halogen analyses (all within 0.3% of the calculated values) were obtained on all compounds used in these radiation studies.

Irradiation Procedure

For the beta irradiations, 50-200 mg of the analytically pure sample was placed in a small watch-shaped container. Because of the hygroscopic nature of all these compounds, transfers from one container to another were carried out in a glove box in an atmosphere of dry nitrogen. The flat sides of the irradiation vessel were 1 cm in diameter, the glass was about 1 mm thick, and the distance between the glass walls was about 2 mm. After the sample was placed in the container it was redried at 100° for several hours under a high vacuum and, finally, the tube was sealed off under vacuum. The irradiations were carried out using the beam of a 2 to 4-Mev linear electron accelerator. The number of electrons passing through the sample was measured by a brass collector (also 1 cm in diameter) placed immediately behind the sample holder; this collector was connected to an ammeter and grounded through a 10^6-ohm resistor. Owing to such factors as the stoppage of some electrons by the sample itself and by the glass walls, scattering of electrons by sample and container, secondary electron emission, and air

ionization, the absolute amount of energy received by the sample is probably not known within a factor of two. However, the comparative values for the various choline analogs are probably correct to within ± 25 percent. Calculations of the energies received by the samples were made as follows:

$$\text{No. of electrons passing through sample} = N = \frac{(\text{amps})\,(\text{secs})}{\text{coulombs/electron}}$$

$$\text{Energy loss in Mev/electron} = \Delta E = \frac{\Delta R}{0.54} \quad \text{(Feather's rule for energies} > 0.8 \text{ Mev)}$$

$$\text{Mev/rep} = (93 \text{ ergs/rep}) \frac{6 \times 10^{23} \text{ ev}}{96{,}500 \times 10^{7} \text{ ergs}} (10^{-6} \text{ Mev/ev}) = 5.2 \times 10^{7}$$

$$\therefore \text{ rep received by sample} = \frac{(N)\,(\Delta E)}{(g)\,(5.2 \times 10^{7})}$$

During the irradiations the samples, which received energy at a rate of approximately 10^7 rep/minute, were kept between room temperature and a maximum of 50° by means of an air blast.

The γ-irradiations were carried out in a 100-curie Co^{60} γ-ray source. Through the use of a ceric ion dosimeter (T. J. Hardwick, Can. J. Chem. 30, 17 (1952)) this source was found to deliver $1.7 \pm 0.3 \times 10^5$ rep/hour. As with the beta-irradiations, all γ-irradiations were carried out on analytically pure anhydrous samples contained in sealed tubes under high vacuum.

Analytical Procedures

Two procedures have been used to determine the extent of decomposition of the irradiated materials: reineckate analysis and paper chromatography.

Reineckate analyses have been used to determine the extent of decomposition of all the choline analogs, with the exception of the trimethyl-3-hydroxypropyl ammonium chloride. In applying this method we have in general followed the procedure of Glick (J. Biol. Chem. 156, 643 (1944)), in which the quaternary ammonium cation is precipitated out of aqueous solution by the anion of ammonium reineckate,

$$NH_4^{+} \; Cr(SCN)_4(NH_3)^{-} .$$

Before the addition of this reagent, our solutions were boiled in 0.1 N KOH solution in order to eliminate any trimethylamine formed by the bombardment, and then neutralized. The precipitated quaternary ammonium reineckate was freed of ammonium reineckate by washing with n-propanol, then dissolved

in acetone, and its concentration was determined by means of its optical density at 526 mμ. The molar extinction coefficient for choline reineckate as determined by Glick was 111; our value is 109. The molar extinction coefficients for the reineckates of choline iodide, trimethyl-2-chloroethyl ammonium chloride, and trimethylethyl ammonium chloride were found to be 111, 111, and 109, respectively; these values are all very nearly the same because the optical density at 526 mμ is due only to the reineckate moiety. Acetylcholine was determined as choline by a prior hydrolysis accomplished by boiling for 15 minutes in dilute aqueous KOH solution.

The reineckate procedure was found to be unsuited for the anlyses of trimethyl-3-hydroxypropyl ammonium chloride, as no procedure could be found that would separate the reineckate of the quaternary ammonium salt from the ammonium reineckate reagent. Propanol washing was found to dissolve large fractions of the desired reineckate along with the unused reagent.

In the analysis of betaine hydrochloride, the titration procedure of Walker and Erlandsen (Anal. Chem. 23, 1309 (1951) was used on the precipitated reineckate instead of the photometric procedure of Glick. In the former procedure, the acid function of the reineckate-precipitated betaine hydrochloride is determined titrimetrically. The presence of trimethylamine was found not to interfere with the Walker and Erlandsen procedure.

Paper chromatography was also used to measure the extent of decomposition of the methyl-labeled choline analogs. This procedure was possible because the only labeled decomposition product found on either two-dimensional (phenol-water and butanol-propionic acid-water) or one-dimensional (butanol-HCl-water) chromatograms was trimethylamine. This product is formed as the hydrochloride (or hydroiodide) during the bombardments; volatile substances formed were never more than 1% (usually less than 0.5%) of the total weight of the bombarded compound. The trimethylamine was identified by and separated from unchanged choline analog by one-dimensional chromatography using the n-butanol-conc. HCl-water solvent (4:1:1 by vol). The position of the radioactive spots was established by radioautography and the amount of trimethylamine hydrochloride determined by counting directly on the paper.

Results

The data are summarized in the Table on the following pages.

Radiation Decomposition of Choline Analogs

Compound	Type of radiation	Rep x 10^{-6}	Percent decomp.	G (molecules decomp / 100 ev)	Method of analysis
Choline chloride	C^{14}-beta	10.7	63	490	Paper chromatorgaphy
" "	2-4-Mev beta	160	51	27	" "
" "	" " "	57 *	16	23	Reineckate
" "	" " "	57	10	15	Paper chromatography
" "	" " "	127	21	14	Reineckate
" "	" " "	66	16	20	"
" "	Co^{60}-γ(1.3 Mev)	37	72	160	Reineckate
" "	" "	28	69	200	"
" "	" "	28	64	190	Paper chromatography
" "	" "	12	25	173	Reineckate
" "	" "	12	22	152	Paper chromatography
Acetylcholine chloride	C^{14}-beta	10.9	< 1	< 6	Paper chromatography
" "	2-4 Mev beta	220	8	2.3	Reineckate
" "	" " "	500	~ 1	~ 0.1	Paper chromatography
" "	" " "	57	1	1.1	Reineckate

Radiation Decomposition of Choline Analogs (cont'd.)

Compound	Type of radiation	Rep x 10^{-6}	Percent decomp.	G (molecules decomp / 100 ev)	Method of analysis
Acetycholine Chloride	2-4-Mev beta	240	16	4	Reineckate
" "	" " "	240	11	3	Paper chromatography
" "	" " "	140	2	0.9	Reineckate
" "	" " "	140	3	1.4	Paper chromatography
" "	Co^{60}-γ (1.3 Mev)	10	~ 0	v. low	Reineckate
" "	" "	10	~ 0	"	Paper chromatography
" "	" "	56	4	5	" "
Choline iodide	2-4-Mev beta	70	6	4.7	Reineckate
" "	" "	240	2	0.4	"
" "	" "	240	5	1.0	Paper chromatography
" "	" "	160	7	2.4	Reineckate
" "	" "	160	2	0.7	Paper chromatography
" "	Co^{60}-γ (1.3 Mev)	15	1	3.4	Reineckate
" "	" "	28	2	3.3	"
" "	" "	16	5	17	"
" "	" "	16	~ 0	v. low	Paper chromatrography

Radiation Decomposition of Choline Analogs (cont'd.)

Compound	Type of radiation	Rep x 10^{-6}	Percent decomp.	G (molecules decomp. / 100 ev)	Method of analysis
$[(CH_3)_3NCH_2CH_2CH_2OH]^+ Cl^-$	2-4-Mev beta	81	3	2.8	Paper chromatography
"	" " "	390	11	1.9	" "
"	Co^{60}-γ (1.3 Mev)	13	1	6	" "
"	" "	27	1	3	" "
$[(CH_3)_3NCH_2CH_2Cl]^+ Cl^-$	2-4-Mev beta	99	5	4	Reineckate
"	" "	101	3	2	"
"	" "	150	1	0.5	"
"	" "	"	10	5	Paper chromatography
"	" "	280	4	1	Reineckate
"	" "	"	28	7	Paper chromatography
"	Co^{60}-γ(1.3 Mev)	16	7	32	Reineckate
"	" "	13	3	17	"
"	" "	12	~ 0	v. low	"
"	" "	"	2	12	Paper chromatography

Radiation Decomposition of Choline Analogs (cont'd.)

Compound	Type of radiation	Rep x 10^{-6}	Percent decomp.	G (molecules decomp. / 100 ev)	Method of analysis
$[(CH_3)_3NCH_2COOH]^+ Cl^-$	2-4-Mev beta	60	14	18	Reineckate
"	" " "	89	13	11	"
"	Co^{60}-γ (1.3 Mev)	60	15	19	"
"	" "	16	4	17	"
$[(CH_3)_3NCH_2CH_3]^+ Cl^-$	2-4-Mev beta	123	3	2.3	"
"	Co^{60}-γ (1.3 Mev)	30	11	34	"

* The braces indicate that the amount of decomposition resulting from a given bombardment was determined independently by the two methods of analysis.

Results and Discussion

The following tentative conclusions have been drawn from this work:

1. The data for choline and acetyl choline indicate that the reineckate and paper-chromatographic methods of analysis give reasonable checks with each other. For some reason as yet unknown these methods are in disagreement in the case of trimethyl-2-chloroethyl ammonium chloride.

2. Choline chloride is by far the most unstable of the seven members of this series studied. Betaine approaches choline in β-instability, but the instability of choline chloride towards γ-radiation is nearly ten times that of betaine, its closest competitor.

3. Analogies with the results of the thermal decomposition of quaternary ammonium bases reported by Ingold (Ann. Reports Chem. Soc. 27, 143 (1930) would indicate that all the quaternary salts studied in this report should be thermally more stable than choline chloride with the exceptions of choline iodide (same degree of stability) and of trimethyl-2-chloroethyl ammonium chloride. This latter compound, because its chloro group has a greater electron affinity than the hydroxyl group of choline, would be expected to have a weaker N-C (ethylene group) bond than is present in choline. However, as regards radiation stability, the N-C bond is actually stronger in the chloro analog than it is in choline. This fact indicates that ionized molecules have a relatively greater role in the radiation decomposition of choline than excited molecules, which would be present in both radiation and thermal decompositions.

4. Whenever the G value is higher than about 3 it is probable that some sort of chain reaction is taking place. Choline chloride and betaine hydrochloride are the only analogs in which this seems definitely to be the case. For all the other irradiations (with the exceptions of the γ-irradiations of trimethyl-2-chloroethyl ammonium chloride and trimethylethyl ammonium chloride) the G values may never exceed 3 to 4.

PHOTOLYSIS OF TRIMETHYLENE DISULFIDE

Robert B. Whitney

The decomposition of trimethylene disulfide by ultraviolet light was studied by Barltrop, Hayes, and Calvin,[1] who showed that the reaction could be followed by observing the decrease in the absorption peak at 3300 Å. The present project is to find out the quantum yield in this decomposition under various conditions, and to see whether visible light can be transferred by suitable dyes to produce the photolysis of trimethylene disulfide.

Direct Photolysis by Ultraviolet Light

Light from a GE reflector sunlamp (275 watts, Hg arc under 2 atmospheres pressure) was passed through a lucite tank through which water circulated. A black brass plate with a 2-inch hole was immersed in the water. A 3-inch Corning No. 9863 filter (maximum transmission at 3400 Å, limits of transmission 2200 to 4200 Å) was used in all cases, and in one experiment an interference filter (Baird Associates, No. 7-1990-C) transmitting at 3658 Å was also used. This transmitted only about one-fourth as much light as the other filter passed.

After the filter, the light passed into a brass chamber with 3-inch quartz windows, through which water at 25° C was circulated from a constant-temperature bath. The photolysis solution was contained in a 1-cm-square quartz Beckman cell of 3.4 cc capacity. A brass mask with a rectangular hole 1/4 in. by 3.4 in. was placed in the water in the chamber, and the Beckman cell was mounted in a spring clip directly against the mask. The light passed through the Beckman cell and into the window of a Kurlbaum large-area bolometer (for description see G. R. Seely[2]), which was 1/2 in. away from the cell. A shutter made from two sheets of black paper protected the bolometer except when readings were being taken.

Two trimethylene disulfide solutions in 80% alcohol were used; one was freshly distilled and the other had remained clear after distillation two months previously. In the photolysis solutions HCl was always used, but in different molar ratios, some less than 1/2 and some greater than 1.

Calculations

On the basis of the value of 147 for the extinction coefficient of the 3300 Å band of trimethylene disulfide, the molar concentration is 0.68×10^{-2} x optical density, since opt. d. = cd, and d = 1 cm. The number of micromoles of disulfide is then 6.8 x opt. d. x cc of solution. Since changes in optical density were around 0.2, and readings can be made to about 0.005, the error in disulfide estimation is about 2.5%.

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1. J. A. Barltrop, P. M. Hayes, and M. Calvin, J. Am. Chem. Soc., in press.

2. Gilbert R. Seely, Photochemistry of Porphyrins (thesis), University of California Radiation Laboratory Report No. UCRL-2417, November, 1953.

Bolometer readings were usually taken at the third position (one scale division equals 7.0×10^{-4} watts). The energy absorbed by the photolysis solution was calculated by subtracting the bolometer reading with the solution in the cell from the bolometer reading with alcohol in the cell. Readings could be made to 0.1 scale division, and since the differences varied from 2.7 down to 0.6, the error in energy measurement varied from about 4% up to 16%. With 3650 Å as the wave length of most of the energy from the sun lamp transmitted by the filter, the number of micromoles of photons absorbed per hour per scale division was:

$$\underbrace{\frac{3.650 \times 10^{-5}}{6.62 \times 10^{-27} \times 3 \times 10^{10}}}_{\text{(photons per erg)}} \; \underbrace{\frac{10^{6}}{6.02 \times 10^{23}}}_{\text{(micromoles per photon)}} \times \underbrace{10^{7}}_{\text{(ergs per hour per watt)}} \times \underbrace{3600 \times 7.0 \times 10^{-4}}_{\text{(watts per scale div.)}} = 7.7.$$

Experimental

After a series of three preliminary photolyses in which suitable conditions were determined and the apparatus was redesigned, three series of experiments were carried out.

Experiment I.

Redistilled trimethylene disulfide, diluted with absolute alcohol. Volume 3.4 cc, containing 42.5 micromoles disulfide; HCl, 10 μmoles, (2.94×10^{-3} M).

Table I

Quantum Yield of Photolysis of Trimethylene Disulfide							
Original concn.	Time (hours)	Change in optical density	μmoles lost	Average bolometer reading	Fraction of incident light absorbed	μmoles of 3650 Å photons absorbed	Quantum yield
1.25×10^{-2}	0.33	0.19	4.4	2.7	0.47	6.93	0.63±0.04
1.12×10^{-2}	0.50	0.26	6.0	2.6	0.45	10.0	0.60±0.04
0.95×10^{-2}	0.50	0.22	5.1	2.3	0.40	8.85	0.58±0.04
0.08×10^{-2}	1.00	0.38	8.8	1.9	0.33	14.6	0.60±0.04
0.54×10^{-2}	2.00	0.42	9.7	1.15	0.20	17.7	0.55±0.06
0.25×10^{-2}	3.67	0.31	7.2	0.4	0.07	11.3	0.64±0.16

Experiment II.

Clear undistilled trimethylene disulfide, diluted with absolute alcohol. Volume 3.35 cc, containing 15.4 micromoles disulfide; HCl, 5 μmoles (1.5×10^{-3} M).

Table II

Quantum Yield of Photolysis of Trimethylene Disulfide							
Original concn.	Time (hours)	Change in optical density	μ moles lost	Average bolometer reading	Fraction of incident light absorbed	μmoles of 3650 Å photons absorbed	Quantum yield
0.46×10^{-2}	1.00	0.21	4.8	1.1	0.21	8.5	0.57±0.07

Experiment III.

Clear undistilled trimethylene disulfide, diluted with absolute alcohol. Volume 3.3 cc, containing 26.6 μmoles disulfide, 30 μmoles HCl (9.1×10^{-3} M). This experiment was performed to check the effect of excess HCl, and the effect of using a very narrow band of spectral energy (interference filter 3658 Å). Also the solution was allowed to stand 39 hours in the dark between the second and third exposures. No change in the absorption occurred.

Table III

Quantum Yield of Photolysis of Trimethylene Disulfide

Original concn.	Time (hours)	Change in optical density	μmoles lost	Average bolometer reading	Fraction of incident light absorbed	μmoles of 3650 Å photons absorbed	Quantum yield
0.81×10^{-2}	1.00	0.36	8.1	2.35	0.42	18.0	0.45±0.03
*0.56×10^{-2}	1.25	0.14	3.1	0.81	0.62	7.8	0.40±0.08
*0.48×10^{-2}	2.05	0.08	1.8	0.25	0.46	4.0	0.45±0.10
0.42×10^{-2}	1.00	0.23	5.2	1.4	0.26	10.8	0.48±0.05

* Light through 3658 Å interference filter.

Conclusions

In the presence of about 1/4 of a molar equivalent of HCl and in about 90% ethanol solution the number of molecules of trimethylene disulfide decomposed per quantum of 3650 Å light is about 0.60, with an error varying from 0.04 to 0.16. Using an initial concentration of HCl of slightly more than 1 mole seems to decrease the quantum yield to slightly below 0.50. The yield seems to be independent of the concentration of disulfide over a wide range, and to be about the same for a narrow band of radiation at 3650 Å as for the wider band produced by the mercury arc under 2 atmospheres pressure and transmitted by the Corning 9863 filter.

Experiments on possible energy transfer by zinc tetraphenyl porphin

Methods for purifying the porphin of ultraviolet-absorbing impurities, and of separating the porphin from trimethylene disulfide, have been worked out. Five different sets of possible photolytic conditions have been tested, and it has been shown that no photolysis occurs. Further experiments are in progress.

ENYZMATIC CARBOXYLATION OF RIBULOSE DIPHOSPHATE

John R. Quayle, R. Clinton Fuller, Andrew A. Benson
and Melvin Calvin

Previous work[1] has indicated that ribulose-1,5-diphosphate acts as the primary carbon dioxide acceptor in photosynthesis. This conclusion was based upon observations with intact photosynthetic organisms. We now wish to report the demonstration of this carboxylation in a cell-free system.

A cell-free preparation was obtained from freshly harvested Chlorella by five minutes' treatment at $2^{\circ} - 5^{\circ}$ in a 9-kc Raytheon oscillator and subsequent removal by centrifugation of cell-wall material and remaining whole cells. It has proved necessary to perform all operations rapidly (20 to 25 minutes from harvest) and in the cold ($< 5^{\circ}$ C) to obtain good fixation. Ribulose diphosphate was isolated from Scenedesmus that were killed rapidly in ethanol after thirty seconds' nitrogen flushing following steady-state photosynthesis in 4% carbon dioxide in air. Such conditions lead to maximum concentrations of ribulose diphosphate.[1] It was isolated from the extract by phenol chromatography of stripes of extract on oxalic acid-washed Whatman No. 4 filter paper, carrying spots of labeled ribulose diphosphate as markers.

Ribulose diphosphate or other substrates were added to the extract and $C^{14}O_2$ was introduced immediately. The results of one-minute exposure to $C^{14}O_2$ are embodied in the following table.

1. J. A. Bassham, A. A. Benson, L. D. Kay, A. Z. Harris, A. T. Wilson, and M. Calvin, J. Am. Chem. Soc. 76, 1760 (1954).

Table IV

Products from One-Minute $C^{14}O_2$[a] Fixation					
	Substrate added 0.1 μmoles				
Products	None	Ribulose-di-P[c,d]	Ribulose-5-P[f]	Ribose-5-P	Fructose-di-P
Phosphoglyceric acid	0[b]	320	0	0	0
Phosphoenol pyruvic acid	0	60	0	0	0
Alanine	0	60	0	0	0
Malic acid	750	80	600	720	900
Aspartic acid	100	10	50	50	40
Citric acid[e]	200	60	250	200	210

(a) Specific activity, 4.8×10^6 cpm/μmole.

(b) Counts per minute measured on paper chromatogram (self-absorption -0.6) fixed during the first minute in 0.2 ml solution containing contents of 10 mg (wet weight) Chlorella cells.

(c) Isolated by water elution from ether-washed paper chromatograms of known amounts of Scenedesmus extracts. The amount, 0.1 μmole, was calculated assuming a cellular concentration of 10^{-3} mole.

(d) It will be noted that fixation with this substrate is markedly lower than with the others. Eluates of a similarly treated blank chromatogram also inhibited fixation because of toxic constituents remaining on the paper (e.g., phenol, quinones, oxalic acid).

(e) In longer fixation periods radioactivity became incorporated in other tricarboxylic acid cycle intermediates (succinic, fumaric, and glutamic acids). No sugar phosphate labeling was observed.

(f) We are indebted to Dr. B. L. Horecker for a sample of ribulose-5-P.

Complementary experiments with labeled ribulose diphosphate and this preparation demonstrated its rapid conversion to free sedoheptulose and a variety of normal metabolic intermediates, which suggests a short lifetime for this substrate, limiting its availability for carboxylation. Similarly, labeled phosphoglycerate was largely converted to alanine in times longer than five minutes at room temperature.

Phosphoglycerate was identified by its chromatographic coordinates and cochromatography of the phosphatased compounds with authentic glyceric acid in four solvent systems. The degradation of the labeled glyceric acid showed 100% radioactivity in the carboxyl carbon,[2] and no detectable activity ($<$ 2%) for the beta carbon.

It is clear that the extracts contain an enzyme (or enzymes) capable of catalyzing the carboxylation of ribulose diphosphate, specifically, to form phosphoglyceric acid. No intermediates between these compounds have been detected by this method, which would have detected as little an amount as that corresponding to 5% of the phosphoglyceric acid formed.

THE EFFECT OF COBALT-60 IRRADIATION ON THE RESPIRATORY METABOLISM OF CERTAIN COMPOUNDS IN MICE

Ann M. Hughes and Melvin Calvin

The effect of total-body irradiation on the liver CoA of mice has been previously reported (Quarterly Report for June, July, and August 1953; and Quarterly Report for September, October, and November 1953). At that time a few preliminary experiments were also carried out on the respiratory metabolism of fatty acids by normal and irradiated mice, on the theory that if the CoA content of the animal were changed by irradiation, there might be a change in the fatty acid metabolism. Recently it was decided to expand this phase of the investigation.

Swiss mice, both male and female, weighing 18–22 g, were used. Co^{60} was used as the radiation source. The mice were placed in a circular lucite container, partitioned so that each mouse had a separate section. The entire cage rotated in the radiation field so that all the animals received equal doses. The distance from the source was so adjusted that the mice received 1300 r total-body irradiation (in one hour of exposure).

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2. We wish to thank Dr. J. A. Bassham of this laboratory for doing the degradations of glyceric acid samples.

Fatty acid metabolism determinations were started either 17 or 41 hours after the completion of the irradiation. For these experiments, the $C^{14}O_2$ breath-line for small animals (as originally described in UCRL-2257, June 25, 1953, and referred to in subsequent quarterly reports) was used. Either $C^{14}H_3COONa$ or $C^{14}H_3(CH_2)_5COONa$ was injected intraperitoneally. The dose of either compound was 1 mg (about 5 μc). In some experiments CoA (2 mg) was also injected intraperitoneally.

The respiratory metabolism of either $C^{14}H_3COONa$ or $C^{14}H_3(CH_2)_5COONa$ 41 hours after irradiation was not appreciably different from the normal.

The $C^{14}O_2$ production from labeled acetate 17 hours after irradiation was depressed about 10%, although there was no change in the heptanoate metabolism in that time. The effect of CoA on fatty acid metabolism was essentially the same in the irradiated and normal mice.

The work is being continued to include the effects of irradiation on the metabolism of glucose and essential amino acids.

THE "COSMIC RAY" EFFECT IN PHOTOMULTIPLIER TUBES

Elton M. Baker and B. M. Tolbert

When two photomultiplier tubes are used in a coincidence circuit to count solid or liquid scintillator samples, a higher background is noted for the two tubes when they can "see" each other than when they are carefully light-shielded from each other. We have observed this phenomenon when the photomultiplier tubes are either facing each other, or at right angles (see Table V).

This phenomenon has been noted by other workers,[1] and since they observed the effect only when the photomultiplier tubes were facing each other, it was called a "light-dark current" and was ascribed to light emission by a sensitive electrode of one of the photomultiplier tubes when electrons were ejected during the normal functioning of the tube.

This increase in background, as noted above, may be explained as due to cosmic ray absorption in materials that are only weakly fluorescent, such as the glass of the photomultiplier tubes. This concept has been verified using extra shielding, glass blank inserts, and other geometrical arrangements, and pulse-height discrimination.

Experimental

Two DuMont photomultiplier tubes[2] were connected to individual preamplifiers and set in a lighttight box, where they could be set either in line facing each other or at right angles. This entire assembly was placed in a deep-freeze unit, which opened from the top and which was maintained at -15°C.

The photomultiplier tubes were operated at 1750 volts between the photocathode and the last dynode. The signal from the preamplifier was sent to a pulse-height discrimination circuit and then to a coincidence circuit. The signals so produced were sent to a second pulse-height discrimination circuit and then were counted on a standard scale of 64.

Results

As indicated in Table V, column 2, the background for the uncovered photomultiplier tubes is approximately the same whether the tubes face each other or are at right angles, and is appreciably larger than when the tubes are covered with black paper. As the tubes can still "see" each other at right angles, this does not disprove the secondary-electron light-emission theory.

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1. F. N. Hayes, R. D. Hiebert, and R. L. Schuch, Science 116, 140 (1952).

2. Allen B. DuMont Laboratories, Inc., Clifton, New Jersey

When a glass block, 2-1/4 in. x 2-1/4 in. x 2-1/2 in., was placed between the tubes, about 100% increase in background count rate was observed, again of comparable value either with the tubes in line or at right angles. Seventy-two hours of light and temperature aging was used to insure against phosphorescent effects in this experiment. Although the ratio of volume of glass in the photomultiplier-tube ends to the total glass with the glass block inserted is about 12 cc to 220 cc, the observed increase in background pulse rate ascribed to glass fluorescence was only from 150 cts/min to 508 cts/min. Since the absorption of light by a block of glass such as this is quite large, this lack of proportionality is not surprising. Also, we are not certain that the fluorescent efficiencies of the two types of glass are the same.

Shielding the photomultiplier tubes and sample box resulted in a significant reduction in the background count rate, which would be expected if cosmic rays were the primary cause for this background phenomenon. Furthermore, an analysis of the pulse heights produced by these photomultiplier tubes with the glass block inserted showed these pulses to be much larger than those derived from the dark current alone, and even to be generally larger than those from C^{14} β-rays in an α-napthylphenyloxazol-giphenyloxazol scintillation toluene solution.

On the basis of these experiments, it is suggested that the increase in background count rate between self-light-shielded and unshielded photomultiplier tubes in coincidence circuit scintillation counting is actually a cosmic-ray background, and should be so called. One factor has not been explored, and that is the contribution of cosmic-ray shower effects on the background of paired, but light-shielded, photomultiplier tubes. This would also be a cosmic-ray background, but rather difficult to distinguish from the normal, dark-current coincidence count rate.

TABLE V

Counting Rate (in cts/5 min) for Two Photomultiplier Tubes in a Coincidence Circuit

	Faces covered	Faces uncovered	Glass block inserted	
			Unshielded	Lead-shielded
Photomultiplier tubes at right angles to each other	1008	1760	3536	2928
	1056	1696	3536	2960
	1024	1776	3616	2992
	960	1744	3424	3056
Average	1012	1744	3528	2984
Photomultiplier tubes facing each other	976	1792	3536	3040
	992	1728	3536	3072
	994	1776	3584	2992
	1040	1760	3568	2960
Average	988	1761	3542	3000

STUDIES ON ADENINE METABOLISM

Edward L. Bennett and Barbara Krueckel

The study of the radioactive acid-soluble compounds obtained in the tissues of C57 male mice after the intraperitoneal administration of adenine-4, 6-C^{14} is nearly completed. One of the primary purposes of this study has been to determine if low-molecular-weight radioactive compounds are present in the cold trichloracetic acid extract that might serve as intermediates in the synthesis of nucleotides or nucleic acids. No evidence for such compounds or for dinucleotides has been found by the procedure used.

As has been described in the previous quarterly progress reports, the cold 10% trichloroacetic acid-soluble fractions of the liver, small intestine, carcass, and kidney were concentrated and partially purified by adorption on Darco G-60 charcoal. Subsequently, the adsorbed material was eluted with pyridine-water and freeze dried. The residue was chromatographed two-dimensionally on Whatman No. 4 filter paper, and by suitable choice of solvent volumes the following compounds were separated: 5-adenylic acid (5-AMP), adenosine diphosphate (ADP), adenosine triphosphate (ATP), inosinic acid (IMP), guanosine monophosphate (GMP), guanosine diphosphate (GDP), guanosine triphosphate (GTP), and diphosphopyridine nucleotide (DPN). A small amount of an adenine-containing compound was found in the same area as GTP, possibly triphosphopyridine nucleotide (TPN).

These compounds were separately eluted, hydrolyzed with HCl, and rechromatographed. The purine (adenine, guanine, or hypoxanthine), obtained upon rechromatography of the hydrolyzed nucleotide, was eluted and the specific activity was determined by counting an aliquot of the eluted spot and determining the concentration of the purine in a separate aliquot by suitable enzymatic spectrophotometric methods.

The specific activities obtained for the soluble nucleotides are given in Table VI. The specific activity of the guanine is calculated to an equivalent weight of adenine so that the specific activity may be directly compared with that of the adenine-containing nucleotides. The precision of the specific-activity determination of the guanine is somewhat lower than that of the adenine nucleotides, as the total quantity of the guanine present was small and the specific activity was relatively low.

In Table VI, the "total 5-AMP" represents the 5-adenylic acid obtained upon hydrolysis of the cold TCA extract with $Ca(OH)_2$ and subsequent chromatography and estimation with muscle deaminase. The adenine obtained from the separated hydrolyzed nucleotides was estimated with xanthine oxidase.

The data obtained for the liver and small-intestine nucleotides indicate that the adenine is rapidly equilibrated between AMP, ADP, and ATP. However, the adenine is incorporated into DPN and TPN (?) at a somewhat slower rate, so that at the short time intervals after administration of the adenine, the specific activity of the adenine in DPN is significantly less than that in the AMP, ADP, and ATP. The equilibrium in the kidney between the nucleotides appears to be slightly less rapid. At first glance, it would appear that adenine is not rapidly equilibrated between AMP, ADP, and ATP in the carcass. However, the nucleotides of the "carcass" are derived from both the bone marrow and the muscle. It is probable that the ADP and ATP values represent primarily the adenylic acid of the muscle, while the higher value for 5-AMP represents primarily the bone-marrow nucleotide. It should be noted that for this tissue, also, the specific activity of the DPN is lower than the nucleotides at 1/2 hour and 2 hours.

The data for the guanylic acid derivatives are rather limited, because such a small amount is present in the tissues. It would appear, however, on the basis of this single experiment, that the specific activity of guanylic acid derivatives is always significantly lower than that for the adenylic acid derivatives of the corresponding tissue. The guanylic acid specific activity of the carcass most nearly approaches the specific activity of the adenylic acid derivatives, but it should be borne in mind that two tissues, muscle and bone marrow, are really involved here. It would seem reasonable that the guanylic acid is derived primarily from the bone marrow, so its specific activity should be compared to that of the 5-AMP of the carcass (believed to be more representative of the bone marrow nucleotide activity), rather than the ADP and ATP. In the small intestine and liver at short time intervals after administration of the adenine, the specific activity of the guanosine triphosphate appears to be higher than the guanosine monophosphate, suggesting the possibility that the adenine is converted to guanine while at the riboside triphosphate level. Further experiments will have to be done to check this observation.

In Table VI are also listed the specific activities of the hypoxanthine derived from the inosinic acid. The specific activities (with one exception; small intestine at one-half hour) are approximately equal to or less than that of the 5-AMP, which is consistent with the idea that the inosinic acid is derived from the adenylic acid rather than vice versa. In addition, it was noted on numerous chromatograms than the total amount of inosinic acid present was larger at 1/2 hour and 2 hours than at 24 hours, indicating that the adenine administered was not truly "tracer," and caused the formation of an increased amount of inosinic acid.

From other chromatograms of the lyophilized cold TCA extracts, the amount and specific activity of the free adenine and hypoxanthine have been determined. In several tissues, the specific activity of the hypoxanthine is greater than that of the isosinic acid or adenylic acid, indicating that a direct conversion of the adenine to hypoxanthine may occur. However, the quantity of hypoxanthine present is small at all times. (The specific activity of the hypoxanthine at 1/2 hour is subject to revision.) Since the hypoxanthine present at 24 hours still has a high specific activity, it is not believed that the adenine goes to hypoxanthine and then to a nucleotide as a main pathway. The specific activity of the adenine appears to decrease in the tissues after

injection of the adenine, indicating that a small amount of free adenine is formed in the mouse. However, the total quantity present is very small. Also shown in Table VI are the specific activities of the DNA- and PNA-adenine of the tissues studied.

There remain about six other radioactive spots on the chromatograms from the acid-soluble extracts which have not been completely identified. One, a major one in the cold TCA extract of the kidney, is believed to be allantoin. The other radioactive compounds comprise only a minor percentage of the acid-soluble material, the major acid-soluble material being the nucleotides (at 2 and 24 hours) and the nucleotides and adenine at 1/2 hour after administration of the adenine-4, 6-C^{14}. Efforts are being made to identify these compounds.

The data obtained in this experiment are consistent with the view that some adenine is incorporated into the nucleic acids by an essentially direct route, while other adenine is incorporated through the 5-adenylic acid pool (note the increase in specific activity in the PNA-adenine from 2 to 24 hours, where no free radioactive adenine is available).

Further studies are in progress with adenine-4, 6-C^{14}.

Table VI

Specific Activity in Dis./μg of Soluble Nucleotides, PNA, and DNA Derived from Adenine-4,6-C^{14} in Mice*						
	Carcass			Small Intestine		
	1/2 hr**	2 hr	24 hr	1/2 hr	2 hr	24 hr
Total "5-AMP"***	156	215	178	1810	3340	1920
5-AMP	425	550	300	2135	3130	2070
DPN	24	108	200	320	1780	1890
ADP	165	224	178	2220	3060	1725
ATP	155	198	197	1950	3440	1145
TPN (?)	148	160	189	420		
IMP	150	155	142	2740	2660	1210
GMP	182 (?)	185	95	190	325	265
GDP	86	138	50	180	400	200
GTP	47	89	53	285	535	190
Hypoxanthine	~1500	1230	645	2520	1960	1150
Adenine	14,000	1430	250	15,000	9350	---
PNA-Adenine	53	186	177	131	375	725
DNA-Adenine	17	117	154	17	120	420

* 1.3 mg. of adenine-4,6-C^{14}, specific activity 17,000 dis./μg, was administered intraperitoneally to male C57 mice. All results are expressed in dis./μg purine, calculated as adenine equivalent.

** Time after administration of adenine-C^{14}.

*** Total "5-AMP" refers to the 5-adenylic acid obtained upon hydrolysis of the cold TCA extract to 5-adenylic acid with $Ca(OH)_2$.

	Liver			Kidneys		
	1/2 hr**	2 hr	24 hr	1/2 hr	2 hr	24 hr
Total "5-AMP"***	820	1690	1500	615	1400	1080
5-AMP	1100	2250	1430	990	1900	1230
DPN	103	645	1585	---	350	1020
ADP	1060	1900	1390	705	1620	1015
ATP	1050	1720	1410	690	1530	960
TPN (?)	250	600	1750	60	295	1250
IMP	825	1540	1100	650	1380	1250
GMP	19	315	330	34	330	530
GDP	20	215	335	---	---	---
GTP	30	180	310	---	---	---
Hypoxanthine	~3000	3240	2760	~ 2000	2610	1480
Adenine	15,500	~2400	~1150	17,300	8200	---
PNA-Adenine	40	150	375	45	215	485
DNA-Adenine	2.4	18	12	< 1	1.4	8.0

* 1.3 mg. of adenine-4,6-C^{14}, specific activity 17,000 dis./μg. was administered intraperitoneally to male C57 mice. All results are expressed in dis./μg purine, calculated as adenine equivalent.

** Time after administration of adenine-C^{14}.

*** Total "5-AMP" refers to the 5-adenylic acid obtained upon hydrolysis of the cold TCA extract to 5-adenylic acid with $Ca(OH)_2$.

SYNTHETIC ORGANIC CHEMISTRY

Patricia Adams, Rosemarie Ostwald and Robert M. Noller

Ethyl-1-C^{14} Iodide

Previous reports from this laboratory (D. E. Pack and B. M. Tolbert, UCRL-1957) have described apparatus and detailed experimental procedures for the preparation of ethyl iodide from sodium acetate by reduction of the acid with lithium aluminum hydride, followed by treatment of the resulting alcohol with concentrated hydriodic acid. In the course of preparing some high-specific-activity ethyl iodide by this method, it was discovered that the yield could be improved from about 70% to 85-95% by the following modification of the method of isolation of the product. Ethanol and concentrated hydriodic acid are heated in a 90° bath, and ethyl iodide is swept continuously out of the reaction mixture as formed with a stream of nitrogen. Following the published procedure, after two hours of nitrogen sweep, the ethyl iodide has been isolated in a liquid nitrogen-cooled trap in 65-70% yield. In our recent experiment, it was found that an additional 15-25% yield can be isolated at this point by reducing the pressure to 0.5 - 0.8 atmos. and continuing the sweep for an additional 1/2 hour. With this simple modification, 50 mc sodium acetate-1-C^{14} (1 mc/millimole) was converted to ethyl-1-C^{14} iodide in two preparations with yields of 83% and 95%, respectively.

Sodium Propionate-2-C^{14} (Patricia Adams and Rosemarie Ostwald)

The 45 mc of ethyl iodide described above was converted to the Grignard reagent and allowed to react with carbon dioxide to give 31.5 mc of sodium propionate-2-C^{14}, sp. act. 1 mc/millimole (70% yield). The preparation from this material of alanine, alanine methyl ester, and leucylalanine with high specific activity is now under way.

Leucyl-alanine-2-C^{14} (Rosemarie Ostwald)

In continuation of work previously reported (Quarterly report, September, October, November 1953) a method for the preparation of leucylalanine was developed. Efforts to modify the synthetic procedure to avoid the appearance of an unknown, radioactive contaminant, tentatively described as a diketopiperazine of leucylalanine, was not successful. The experiments consisted in the hydrogenation of carbobenzoxy-leucylalanine in dioxane or acetone to avoid the possibilities of esterification and consequent formation of diketopiperazine, as was possible in methanol, the solvent previously used. The material thus obtained proved to be a mixture of compounds, of which only a small amount was leucylalanine, as determined by paper chromatography.

The separation of leucylalanine from the contaminating compound was achieved by passage through a column of Dowex 2 or Dowex 50 ion-exchange resin. The water effluent in both cases contained the unknown compound; the hydrochloric acid eluant from the Dowex 2 column and the ammonium hydroxide eluant from the Dowex 50 column contained the pure peptide. The low yield of leucylalanine from alanine methyl ester (20%) has been made more acceptable by the recovery of 40% of the starting alanine by the use of an ion-exchange resin.

4,6-Disubstituted Caproic Acids (Patricia Adams)

In the course of studies directed toward the synthesis of analogs of thioctic acid, some new compounds have been prepared and characterized.

Ethyl 3-(chloroformyl)-propionate was prepared by the method of Riegel and Lilienfeld (J. Am. Chem. Soc. 67, 1273 (1945)). By treatment of this acid chloride with aluminum chloride and ethylene in carbon tetrachloride, there was isolated in 25-30% yield ethyl 4-ketohexenoate-5, bp 90°-93°/9 mm. This product was allowed to react with benzyl mercaptan followed by acid hydrolysis. The product, 4-keto-6-benzylmercapto-hexanoic acid, was isolated in 70% yield. The melting point is 49°-50° C.

Anal. $C_{13}H_{16}O_3S$: Theory: C, 61.9%; H, 6.35%; S, 12.37%.

Found: C, 61.8%; H, 6.42%; S, 12.5%. Melting point of the S-benzyl-thiuronium salt, 127°-128°.

Reduction of this product with sodium borohydride gave a hydroxy acid which could not be induced to crystallize or to form a crystalline S-benzyl-thiuronium salt. The p-toluene sulfonyl ester, however, can be prepared from this oily product. Characterization of this ester is not yet complete.

When the above-described keto acid is treated with benzyl mercaptan and HCl in the presence of zinc chloride, there is isolated in 85-90% yield 4,4,6-tribenzylmercapto-hexanoic acid. This mercaptal precipitates as a white waxy solid, mp 80°-85°. The S-benzyl thiuronium salt was prepared, mp 129°-30°. The melting point of a sample of this salt mixed with the salt of the starting material (mp 127°-128°) was 117°-125°.

Anal. $C_{35}H_{40}S_4O_2N_2$: Theory: C, 64.8%; H, 6.17%; N, 4.32%; S, 19.75%.

Found: C, 65.0%; H, 6.17%; N, 4.45%; S, 19.62%.

According to Soper et al (J. Am. Chem. Soc., in press) the analogous 6,6,8-tribenzylmercapto-octanoic acid can be reduced with sodium in liquid ammonia to yield 6,8-dithioloctanoic acid, which can be isolated in about 15% yield as the cyclic disulfide. Attempts to duplicate this reduction under identical experimental conditions with the mercaptal of hexanoic acid have been unsuccessful. Only 5-10% yield of an ether-soluble acidic oil is isolated in the reduction, the remainder of the product being insoluble polymers. This acidic oil has not yet been identified. Its insolubility in hot hexane plus the absence of an ultraviolet absorption peak around 3300 Å indicates that it cannot be the desired disulfide. Its equivalent weight (175-190) rules out the possibility of its being unreacted starting material. Although attempts to crystallize it have been unsuccessful, its chromatographic behavior indicates it is primarily a single compound.

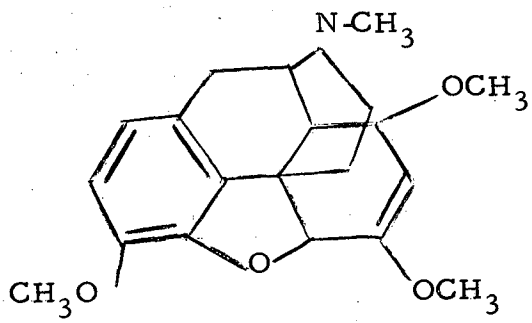
Morphine and Codeine Glucuronides (Helen N. and Henry Rapoport)

Synthetic morphine and codeine glucuronides are desired in order to study and compare their properties with morphine and codeine metabolites that appear to be glucuronides, although their properties are quite different from those of usual glucuronides.

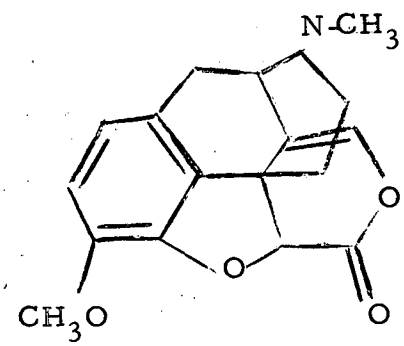
Following the general method for preparing glycosides, a mixture of codeine, methyl 1-bromo-2, 3, 4-triacetyl-α-glucuronate, and silver carbonate was heated under reflux in benzene. Since only about a 10% yield of crude glucuronide was obtained, the reaction was examined in detail and the cause for the low yield was found to be the oxidation of codeine to codeinone to silver carbonate. Further experimentation demonstrated that this conversion to codeine to codeinone by silver carbonate in benzene could be accomplished in 70 – 80% yields, making this process by far the best for preparing codeinone. Other possible applications of oxidation by silver carbonate are being pursued, as well as alternative methods for preparing glucuronides.

Morphine -7-C^{14} (Calvin H. Lovell and Henry Rapoport)

The structure of the compound isolated from the reaction of codeinone with trimethylorthoformate quite definitely seems to be 8-methoxy-Δ^6-dihydrothelaine,



rather than codeinone dimethylketal. Its reaction with osmium tetroxide is being investigated as a means of preparing the desired intermediate,



IRRADIATION DECOMPOSITION OF PURE ORGANIC COMPOUNDS

Robert M. Noller and Bert M. Tolbert

An accurate picture of the interaction of ionizing radiation with organic molecules is of fundamental importance to the field of irradiation chemistry. Up to the present time the information available on the irradiation chemistry of pure organic compounds is relatively meager. Much of the work that has been done is empirical and ofttimes deals with complex systems, such as plastics, pharmaceuticals, and biological products. The nature of these systems is such that it is difficult to determine any generalizations from the radiation decomposition data obtained.

The decomposition of organic compounds in aqueous systems has also been rather extensively studied, and this has led to a fundamental understanding of the mechanism of the interaction of ionizing radiation with water and of the free radicals thus produced with the organic compounds. However, the interaction of the radiation with the organic molecules themselves has remained a moot question; since it is such a minor fraction of the total effect. Therefore, we are undertaking a simple program to irradiate a series of pure organic compounds with γ- and β-rays to determine the percent decomposition for a given radiation dosage and to determine the major products of decomposition.

Experimental Procedure

Samples of about 1 g in weight are placed in a sealed evacuated glass break-off tube and are irradiated in a 100-curie Co^{60} source, which presently delivers about 2.9×10^5 r/hr. After the irradiation, the gaseous decomposition products are separated into a non-liquid-nitrogen-condensible fraction, a liquid-nitrogen-condensible fraction, and a dry-ice-condensible fraction. The gaseous fractions are then transferred by means of an automatic Toepler pump system to a gas burette, where three volumes are measured. The samples are then transferred to gas-sample bottles and are analyzed with a mass spectrometer.

The sample is then analyzed by isotopic dilution, using labeling with carbon-14 to determine the percentage of the original material still remaining in the irradiated compound. The specific-activity analyses are currently being performed using oxidation of the sample with the Van Slyke-Folch oxidation mixture and direct introduction of the resulting CO_2 into an ionization chamber. The precision of these analyses is in the order of magnitude of 0.5%. Thus, it is necessary to have decomposed the sample to about 10% in order to know the extent of decomposition to a precision of 10%.

Results

At present, techniques involved in these measurements are being checked, using the irradiation of benzoic-carboxyl-C^{14} acid. This solid is particularly convenient for irradiation studies because the material may be easily sublimed, and this gives a chance for the gaseous decomposition products entrapped in the crystalline structure to be released. Liquids can also be relatively easily handled by this technique. Preliminary results on the gaseous products

from one sample of benzoinc acid, which received 3.88×10^{19} electron volts in energy/mmole from the Co^{60} source (approximately 4×10^7 rep), showed the following quantity of compounds per mmole of benzoic acid: Noncondensable in liquid nitrogen -- CH_4, 1.6×10^{-6} mmole; H_2, 23.3×10^{-6} mmole; CO, 168×10^{-6} mmole. Condensable in liquid nitrogen -- C_2H_6, 2.9×10^{-6} mmole; C_6H_6, 40.2×10^{-6} mmole; CO_2, 1810×10^{-6} mmole. A preliminary G value of the decarboxylation of benzoic acid may be calculated using the sum of the quantities of CO_2 and CO collected.

This value is

$$G_{CO_2 + CO} = \frac{(19.8 \times 10^{-7})(6.02 \times 10^{23})\,10^2}{3.88 \times 10^{19}} = 3.07$$

The presence of ethane in these gaseous products is rather surprising, and it may be due to extraneous sources. Another sample of benzoic acid is now being analyzed, and material is also being prepared for irradiation of naphthoic acid.

RATE STUDIES IN PHOTOSYNTHESIS

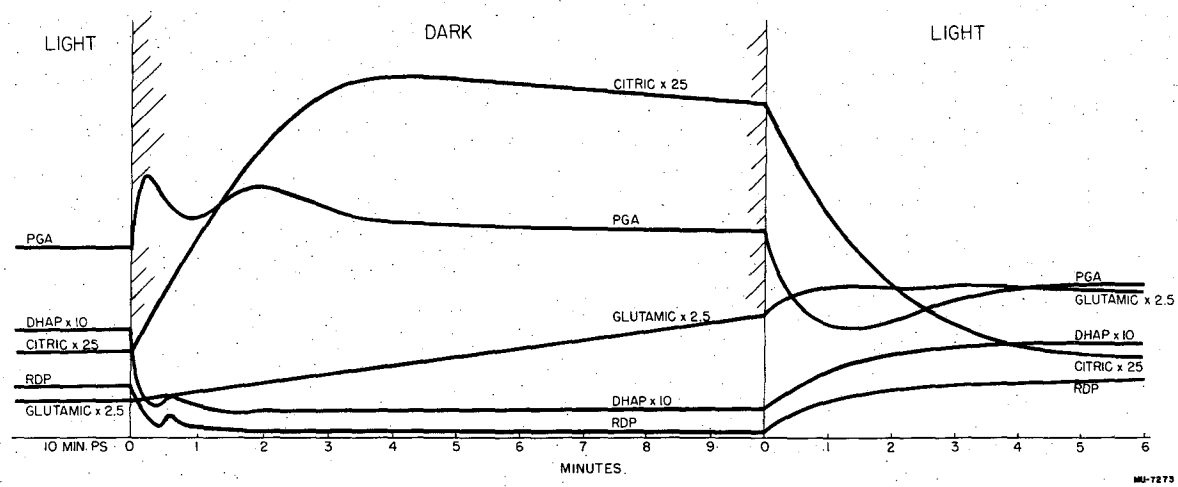
James A. Bassham and Andres O. M. Stoppani

The effect of sudden cessation of illumination on the steady-state concentrations of photosynthetic intermediates was studied by Calvin and Massini.[1] Since that time the techniques for studying the changing concentrations of these compounds in algae while changing only one external variable have been improved by Wilson[2] so that it seemed desirable to repeat the light-and-dark experiment using the improved techniques.

This experiment has been carried out and the changing concentrations of some photosynthetic and respiratory intermediates determined as before by paper chromatography. The results are shown in Fig. 1, where concentrations are plotted as a function of time in dark and light. The experiment in this case was carried out at 4°C, at which temperature the over all rate of photosynthesis is only about one-fourth the rate at room temperature. It is seen that the concentration of phosphoglyceric acid (PGA) rises in the dark and drops in the light, while the concentration of ribulose diphosphate (RDP) drops in the dark and rises in the light. Both effects were reported by Massini[1], though for the light-to-dark transition only. Furthermore, it is seen that the concentration of DHAP (triose phosphate), the product of reduction of PGA, falls in the dark and rises in the light. These results are consistent with the carbon dioxide reduction cycle proposed in a previous paper,[3] and further substantiate the belief that light energy is needed in the step involving reduction of PGA and perhaps in the step involving formation of RDP. The latter light requirement, if true, may indicate that ATP is required for the formation of RDP from ribulose monophosphate and that the ATP level is higher in the light than in the dark.

1. M. Calvin and P. Massini, Experientia 8, 445 (1952).
2. A. T. Wilson, Thesis, University of California, 1954.
3. J. A. Bassham, A. A. Benson, L. D. Kay, A. Z. Harris, A. T. Wilson, and M. Calvin, J. Am. Chem. Soc. 76, 1760 (1954).

The great relative increase in citric acid level in the dark is consistent with previous proposals that one of the actions of light is the blocking of pyruvic acid oxidase through the conversion of thioctic acid to its dithiol. This would lead to a decrease in the concentration of acetyl CoA available for condensation with oxaloacetic acid to form citric acid, so that in the light the steady-state concentration of citric acid should become less than its concentration in the dark.


LIGHT
DARK
LIGHT
CITRIC x 25
PGA
PGA
DHAP x 10
CITRIC x 25
RDP
GLUTAMIC x 2.5
GLUTAMIC x 2.5
DHAP x 10
RDP
PGA
GLUTAMIC x 2.5
DHAP x 10
CITRIC x 25
RDP
10 MIN. PS
0 1 2 3 4 5 6 7 8 9 0 1 2 3 4 5 6
MINUTES.
MU-7273

- Fig. 1 -

RESPIRATORY METABOLISM OF LABELED ORGANIC COMPOUNDS

Martha Kirk and Bert M. Tolbert

In the last quarterly report (UCRL-2531, April 1, 1954), an instrument was described that permitted the continuous analysis of the respiratory carbon dioxide from experimental animals that had been given doses of radioactive compounds. This instrument continuously determines the total C^{14}, CO_2 and the specific activity of the C^{14} (i.e. $\frac{C^{14}}{CO_2}$), and records the data on a multichannel analyzer.

Rate studies have now been made using sodium acetate-2-C^{14}, glucose-C_6^{14}, glycine-2-C^{14}, leucine-3-C^{14}, and glyceryl-tripalmitate-1-C_3^{14}. The results of partial analyses of the rate curves obtained are given in Table VII. The data presented in this table include a variety of experimental conditions and test procedures. Some of the major variations that we have been investigating have included the size of the ionization chamber used, the evaluation of the dynamic time constants of the analyzing instruments, and variation in injected dose.

TABLE VII.

Summary of C^{14}, CO_2 Metabolism Data on Animals Injected with Various C^{14}-Labeled Compounds

Compound	Animal	Date (1954)	% C^{14} recovery in 7 hours	Time of total C^{14} peak, min.	Time of sp. act. peak, min.	Remarks
$C^{14}H_3COONa$	Rat	3/8	63.90	20	22	Initial experimental runs. Flow rates not checked with wet test meter.
"	"	3/9	52.72	13	17-18	
"	"	3/10	53.14	20	26	
"	"	4/21	95.26	15	20	
"	"	4/30	68.73	10	17-20	Actually run 9 hrs. Sp. act. good even on 10^{13}-ohm resistor.
"	"	5/3	63.24	11	19-22	Sp. act. good; α's showing.
"	"	5/31	103.1	Indefinite 11-38	Rounded 24	0.16 mg acetate injected in 0.2 ml.
"	"	6/7	70.21	12-38	Rounded 28	14 mg. acetate injected in 0.2 ml.
Glucose-C_6^{14}	"	5/10	63.07	20-43	40	Total act. levels off at max. Sp. act. peak definite. Sp. act. curve good. 0.1 mg inj.
"	"	5/11	59.74	36	45-47	2 mg inj.
"	"	5/24	64.17	33	30	0.1 mg inj. [a]One-liter ion chamber[b]
Glycine-2-C^{14}	"	5/19	10.65	25	33	One-liter ion chamber
"	"	5/21	15.70	24.5	30	" " " "
"	"	5/26	9.22	46	30	" " " "

Compound	Animal	Data (1954)	% C^{14} recovery in 7 hours	Time of total C^{14} peak, min.	Time of sp. act. peak, min.	Remarks
Glycine-2-C^{14}	Rat	5/27	11.90	35.6	27-30	One-liter ion chamber
Leucine-3-C^{14}	"	5/4	27.98	87	50-62	
	"	5/7	29.99	42	45-52	
Glyceryl-tripalmitate-1-C^{14}	Atherosclerotic rabbit	4/22	12.52[c]	Levels off at	- 90 min.	
"	"	4/23	9.57[c]	" " "	- 70 min.	100 mg heparin also injected
"	"	5/5	4.49[c]	" " "	- 10-20 min.[d]	100 mg heparin also injected
"	"	5/6	5.70[c]	" " "	- 20 min.[d]	

(a) Animal replaced in line at 8:30 A.M. Results were quite measurable. Injection of 200 mg glucose at 29.5 hr after initial injection made no permanent difference in excretion rate. Rate during second day ranged from 0.5 to 0.25%/hr.

(b) One-liter ion chamber. All other results were obtained using a 250-cc. ionization chamber.

(c) Percent recovery in 6 hours only.

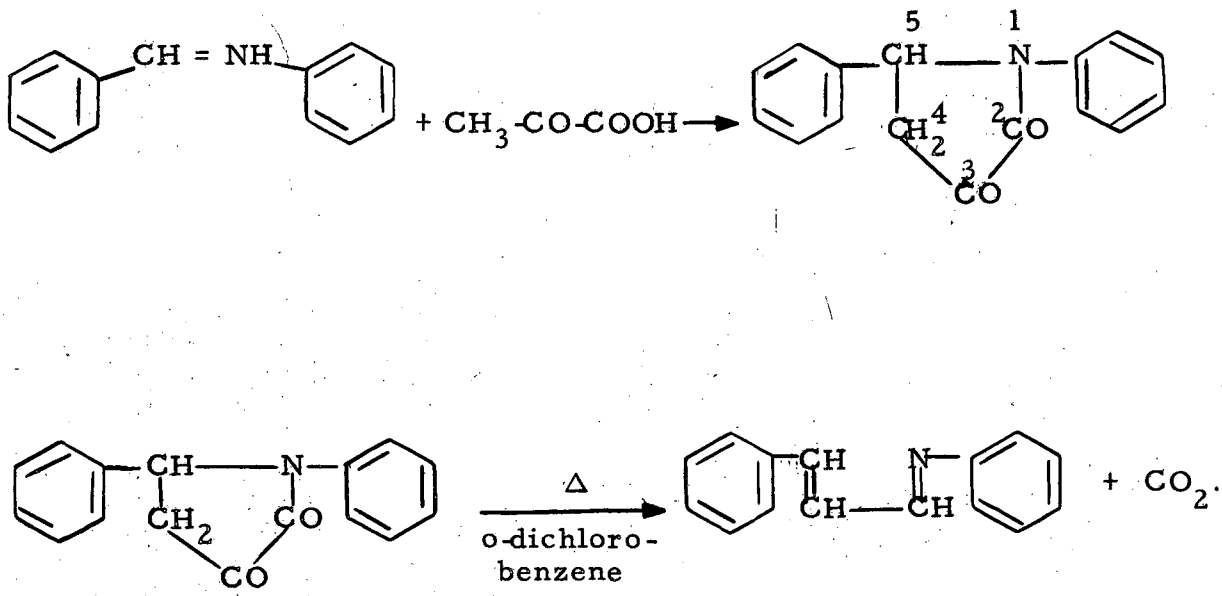
(d) Rabbits run on 5/5 and 5/6 were still eliminating measurable amounts of radioactivity one week after last injection.

STUDY OF A REACTION MECHANISM

Paul Vercier

Introduction

1, 5-Diphenyl-2, 3 pyrrolidinedione (DPPD), obtained by heating pyruvic acid and benzylidine aniline, gives CO_2 and an anil when heated in o-dichlorobenzene.[1]



The problem is, then, to know from which carbon atom of the molecule comes the CO_2 -- 2 or 3?

It seemed that the labeling of the pyruvic acid with C^{14} in the carbonyl position could provide a satisfactory answer to that question, providing that the label is in the 3-position of the pyrrolidinedione molecule. So, before starting on the mechanism problem, we had to prepare the labeled DPPD and, to be absolutely sure that the label is really in position 3, degrade the DPPD molecule.

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1. Vaughan and Peters, J. Org. Chem. 18, 389 (1953).

Preparation of the DPPD

DPPD was made according to the procedure of Bucherer and Russischwili.[2] To a solution of 9.05 g (50 mmoles) of benzaniline in about 100 ml of glacial acetic acid, cooled at 8°C, one adds slowly 4.4 g (50 mmoles) of pyruvic acid dissolved in 10–12 ml of absolute ether with constant stirring. After a while, a precipitate is produced; one keeps on stirring for 15 more minutes, and dilutes with four or five times the quantity of water, whereby a precipitate is formed. It is then separated, washed with water, and air dried. Yield: 9 g, 80%.

The purification was made according to (1): crystallization from hot absolute alcohol. The crystals were then washed with cold absolute alcohol until all color had disappeared; mp 158.5° (dec.).

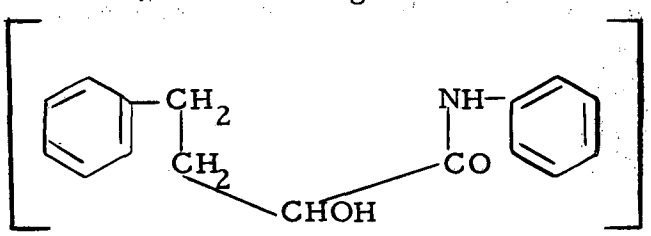
Degradation of the DPPD

As DPPD is quite an unstable product, easily oxidized in solution in the presence of air and therefore rather difficult to work with, it was thought that a more stable form, such as the hydrogenation product of DPPD, would be a better raw material to degrade.

Hydrogenation. 246 mg (~1 mmole) of DPPD was dissolved in 35 ml of methyl acetate, to which was added 100 mg of palladium-on-charcoal (30%), and hydrogenated at atmospheric pressure. Two molecules of H_2 were taken readily; then the uptake stopped. The solution was filtered, the solvent evaporated to dryness, and the residue dissolved in absolute alcohol, from which a crystalline product is precipitated by adding a few drops of water.

Properties of the Hydrogenated Compound. The crude material becomes yellow at 172° C and melts without decomposition at 173° – 74° C. It is rather difficult to recrystallize, being slightly soluble in hot water, alcohol, ether, chloroform, benzene, and ethyl acetate. In a warm concentrated solution of 12 N HCl, the compound is soluble and comes out upon cooling in the form of white crystalline needles (a). When these crystals are put on an already hot melting-point apparatus they decompose, with evolution of gas and further solidification. This phenomenon is observed down to 140°C. The white product left behind melts cleanly without decomposition and without getting yellow at 198°C. But if one places the crystals of the hydrogenated compound a on the cold block and heats them slowly, then they turn yellow around 173°C and melt around 174°C.

Since the hydrogenation showed evidence of an uptake of 2 mmoles of hydrogen, one can assume that one of the moles of H_2 was used for the ring opening and the other one for the reduction of one of the carbonyl groups. After treatment with hot concentrated HCl solution, one should get



After drying in vacuo at 50°C for three hours, analytical results were:
Calc: C, 65.85%; H, 6.21%; N, 4.80%. Obs: C, 65,35%; H, 6.12%; N, 5.02%.

The same crystals a were then washed with water until the solution showed no more Cl^- ion in the solution with $AgNO_3$. During this process, they lost their shape and gave an amorphous compound, melting around 200°C.

The hydrogenated DPPD is soluble in cold 10% NaOH solution, from which it did not come out by further dilution. It was thought that it would be possible to isolate an amide and then chop off one of the two carbonyl carbons in the molecule.

One gram of hydrogenated DPPD was dissolved in 11 ml of 10% NaOH solution, and boiled under reflux for one hour. No change in color occurred during the reaction. After cooling, the mixture was extracted with ether. Three layers were formed: The ether layer gave on evaporation some yellow crystals, presumably the starting material. The colorless water layer gave, upon neutralization with dilute HCl, 0.14 g of a white precipitate, mp 183° – 85°C. The layer in between, dark yellow, gave by evaporation 0.5 g of a solid melting at 290°C and then solidifying again.

A chromatogram on a silica column with $CHCl_3$ failed to bring any separation of the hydrogenated DPPD or to give a sharp-melting compound. Because of the considerable amount of work involved in the identification of the various compounds, this part was set aside.

Thermal Decomposition of DPPD

Another approach to the problem consists in just a qualitative experiment. Starting from a 3-labeled compound (assuming that the label is in this position), dissolving it in o-dichlorobenzene and heating the solution, it is possible to check the activity of the evolving CO_2. If the CO_2 is inactive, then it comes from carbon 2 of DPPD. If the CO_2 is active, and the specific activity the same as in the starting material, then it comes from carbon 3. If the CO_2 is active, but the specific activity is different from the starting material, then the mechanism is more complex.

A quantitative run was made first to check how many molecules of CO_2 are evolved by heating.

Results of three experiments were as follows:

30 min heating at 138° C, 80% CO_2 evolved;

45 min heating at 138° C, 81.5% CO_2 evolved;

65 min heating at 141° C, 81.5% CO_2 evolved.

This is the present status of results on this experiment.

NUCLEAR CHEMISTRY

Glenn T. Seaborg and Isadore Perlman

BISMUTH-207

Donald Strominger

The gamma-ray spectrum of the electron-capture decay of Bi^{207} to Pb^{207} was reinvestigated here by scintillation spectroscopy on a sample more than four years old. Gamma rays of 0.56, 0.75, 1.1, and 1.76 Mev were seen. The 0.56- and 1.1-Mev gamma rays have been reported previously[1,2,3,4,5] and their position in the decay scheme of Pb^{207} is well established.[2,4]

McGowan[4] and Wapstra[5] by gamma-scintillation spectroscopy also reported a gamma ray of energy around 1.75 Mev. They attributed this gamma ray to isotopes other than Bi^{207} because it decayed with a shorter ($\geq$ 300 days[5]) half life than that of Bi^{207}.

McGowan[4] also saw a gamma ray of about 0.7 Mev, which probably corresponds to the 0.75-Mev gamma ray seen here.

Coincidence studies of the 0.75- and 1.76-Mev gamma rays with the 0.56-Mev gamma ray are in progress to determine their proper relationship to the decay scheme of Bi^{207}.

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1. H. M. Neumann and I. Perlman, Phys. Rev. 81, 958 (1951).
2. G. Friedlander, E. Wilson, A. Ghiorso, and I. Perlman, Phys. Rev. 91, 498 (1953).
3. D. E. Alburger, Phys. Rev. 92, 1257 (1953).
4. F. K. McGowan and E. C. Campbell, Phys. Rev. 92, 523 (1953).
5. A. H. Wapstra (dissertation), University of Amsterdam (1953).

NEUTRON-DEFICIENT PLATINUM, GOLD, AND MERCURY ISOTOPES

Warren G. Smith and Jack M. Hollander

Based upon previous assignments, namely, Pt^{191}, Ir^{189}, Pt^{187}, Ir^{188}, and Ir^{187} as shown in brackets in the table, the following tentative assignments have been made: Au^{187}, Au^{188}, Au^{189}, Au^{190}, Pt^{189}.

Hg	188	189	190	191 (55 m) 55 m	192		
Au	187 17 m	188 10 m	189 40 m	190 40 m	191 3 h (10 h) 3 h 14 h	192	
Pt		187 3 h 26 h	188 11 d 11 d	189 11 h	190	191 (3 d)	192
Ir			187 (12 h)	188 (41 h)	189 (>100 d) 11 d	190 (3 h) (12 d)	191

The general character of all the experiments was to bombard a given Z element with 100–130 protons, separate the Z + 1 element, and milk the daughter of the Z + 1 element. Usually a small fraction of the Z + 1 element was prepared for direct Geiger counting.

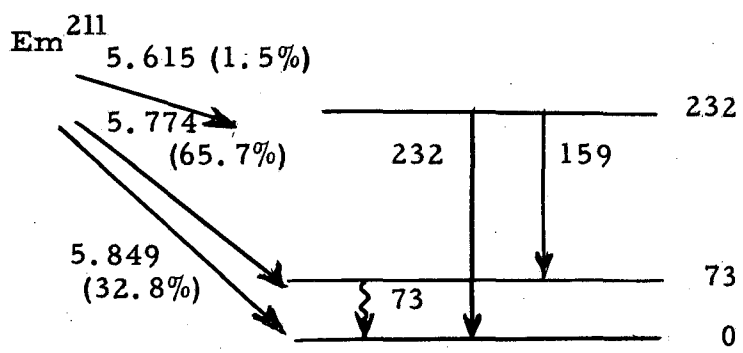
FURTHER INVESTIGATION OF THE ALPHA SPECTRUM OF EMANATION-211.

Allan W. Stoner, Earl K. Hyde, and Frank Asaro

The alpha fine structure of Em^{211} had been previously reported to consist of a 5.847-Mev alpha group in 33% abundance and a 5.778-Mev alpha group in 67% abundance.[1] In the September-November quarterly report we published the observation of three gamma rays in coincidence with the alpha particles of Em^{211}.[2] From the above groups only one gamma ray can be accounted for, which makes the postulation of one or two additional alpha groups necessary to explain the coincidence of gamma rays. This report covers our further attempts to clarify the decay scheme by looking for the alpha particles by use of the alpha-ray spectrograph.

A sample of Em^{211} was prepared by spallation of thorium with 340-Mev protons and collection on aluminum by the glow-discharge technique.[1] The alpha-particle energies were then analyzed in the magnetic alpha-ray spectrograph. The energy and intensity of the groups can be determined from the position and number of alpha tracks on the photographic plate.

In the alpha-gamma coincidence studies, the two gamma rays requiring additional alpha groups for their explanation were 154 and 224 kev energy. In counting the alpha tracks on the plate we looked in the general area where alpha particles giving rise to these gamma rays would be expected to appear. We found one alpha group of 5.615 ± 0.005 Mev whose intensity was 1.5%. This group is sufficient to explain the appearance of both gamma rays. No other alpha groups with intensity greater than 0.5% were found in the region from the ground state to about 500 kev above it. The alpha-decay scheme for the isotope, as completely as it has been determined by us, is given below.



1. As reported by Floyd F. Momyer , Studies of Neutron-Deficient Isotopes of Emanation, Francium, and Radium, (thesis), University of California Radiation Laboratory Report No. UCRL-2060 (February 1953).

2. Quarterly report, September, October, November, 1953, UCRL-2455.

EMANATION ISOTOPES FROM GOLD

Allan W. Stoner and Earl K. Hyde

In order to investigate the nuclear properties of the neutron-deficient isotopes of emanation, 5-mil gold foil was bombarded in both air-and-water-cooled target setups in the 60-inch Crocker Laboratory cyclotron with nitrogen ions. The emanation was separated from the target by amalgamating it with mercury by induction heating in a vacuum line, and then collecting the emanation in liquid N_2 traps. The meanation was affixed to aluminum foils by the glow-discharge technique.[1] The samples were studied in the alpha-pulse analyzer in order to determine the alpha energies, and the decay of the peaks was followed for half-life determination.

In the first alpha-pulse analysis (Fig. 1) two peaks were found. The energies of these two groups, when compared to Cm^{242}, Cm^{244}, and Ra^{226} alpha groups, were determined to be 6.12 and 6.24 Mev.

The decay of the 6.12-Mev peak indicated two components of half lives of 23 minutes and 10 to 11 minutes, respectively, which were assigned to Em^{208} and Em^{207}. The 6.22-Mev peak decayed with a 5 to 6-minute half life, and was assigned to Em^{206}. With less certainty a 3-minute decay was observed at 6.27 to 6.30 Mev. The mass assignments are based largely on the identification of the daughter products. Alpha activity of 1.7-hour At^{207} was observed to grow in from a 10-minute parent, thus identifying the 10-minute 6.12-Mev alpha activity as Em^{207}. Alpha activity of 52-minute Po^{202} was observed to grow in from a 6-minute parent. This identifies the 6-minute 6.22-Mev alpha activity as Em^{206}.

Figure 2 shows an alpha spectrum taken some time after preparation of an emanation sample, showing At^{207} and Po^{202} daughter activity. Some alpha activity due to 9-day Po^{206} was observed in long runs on the pulse-height analyzer.

The alpha-electron capture branching ratios for Em^{207}, Em^{206}, and Po^{202} can be calculated from these experiments. For Em^{207}, by calculating the Em^{207} atoms required to yield the experimentally determined At^{207} activity at any time and then comparing this number to the alpha counting rate of Em^{207}, the alpha-electron capture branching ratio can be found. The decay was determined to be 4% alpha and 95% electron capture. In this calculation, the alpha branching of At^{207} was taken as 10%. For Em^{206}, the activity of Po^{206} was measured and, on the assumption of a 5% alpha branching ratio for Po^{206}, the number of atoms of Em^{206} was calculated and compared to the alpha activity of the Em^{206} to yield a 30% electron capture and 70% alpha branching ratio. The Po^{202} alpha activity was compared to the number of atoms of Po^{202} formed by the Em^{206} alpha activity, and a value of 2% alpha and 98% electron capture for Po^{202} was determined.

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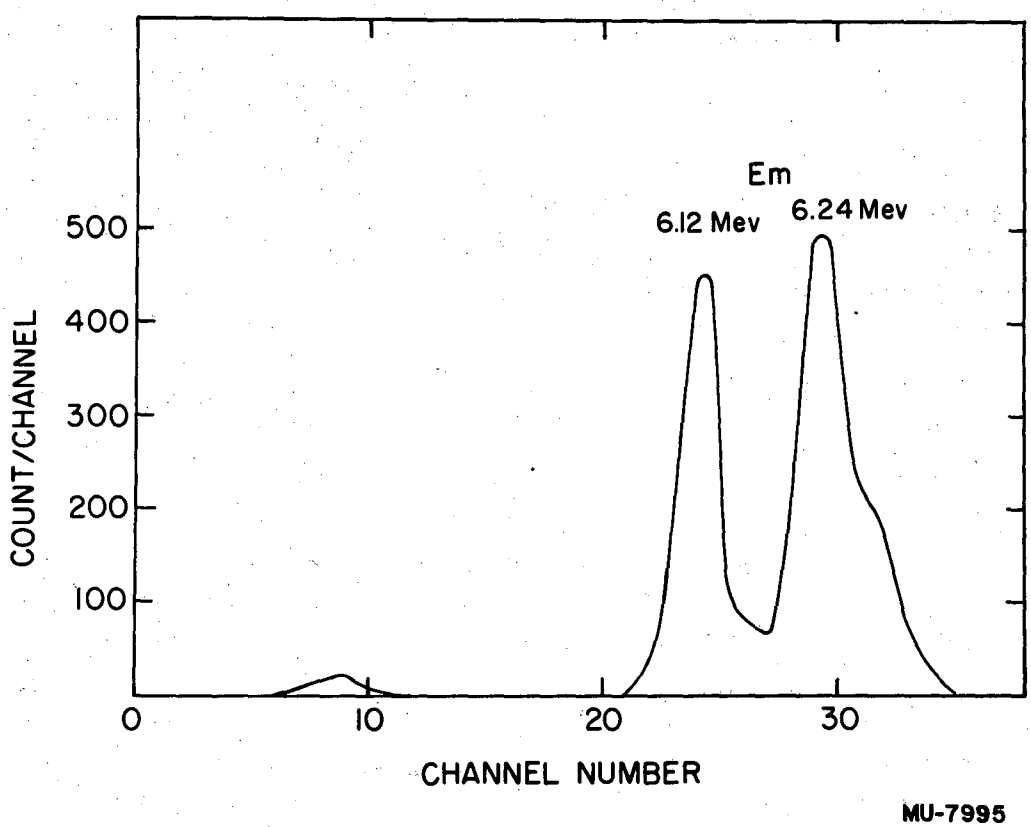
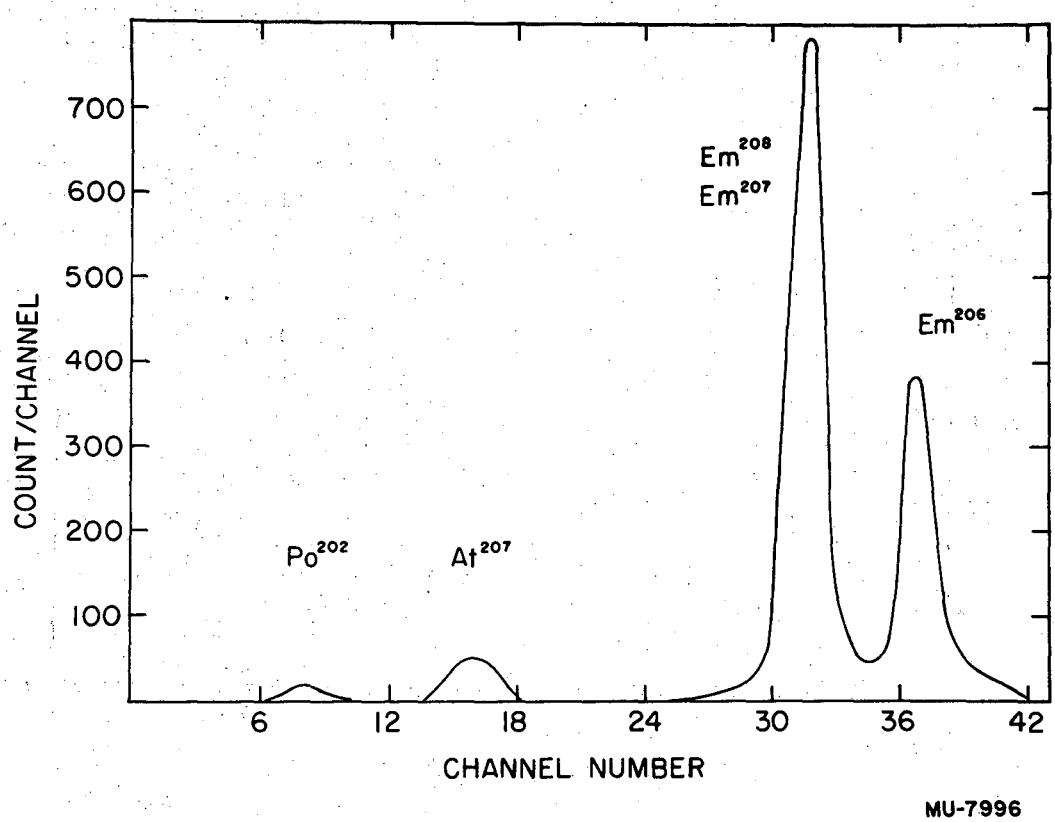
1. Floyd F. Momyer, Studies of Neutron-Deficient Isotopes of Emanation, Francium, and Radium Laboratory Report No. UCRL-2060 (February, 1953).


Em
6.12 Mev
6.24 Mev
500
400
300
200
100
COUNT/CHANNEL
0
10
20
30
CHANNEL NUMBER
MU-7995

- Fig. 1 -


700
600
500
400
300
200
100
COUNT/CHANNEL
Po202
At207
Em208
Em207
Em206
6
12
18
24
30
36
42
CHANNEL NUMBER
MU-7996

- Fig. 2 -

The half lives and alpha energies for Em^{207} and Em^{206} reported here are in agreement with some work of the same type of bombardment by W. E. Burcham in Birmingham, England.[2] A summary of all half lives and alpha energies determined in these experiments is given below.

	$t_{1/2}$	E_α	Branching ratio
Em^{208}	21 min	6.12	
Em^{207}	11 min	6.12	3.5%α, 96.5% EC
Em^{206}	6.25 min	6.22	70%α, 30% EC
Em^{204}	3 min	6.27 - 6.30	
Po^{202}	52 min	5.60	2%α, 98% EC
At^{207}	106 min	5.75	

2. Private communication, W. E. Burcham to G. T. Seaborg, now in publication.

BETA DECAY OF NEPTUNIUM-238

John O. Rasmussen, Jr.

Beta spectroscopic work on Np^{238} has been reported by Freedman, Jaffey, and Wagner.[1]

A considerable amount of work has been done in the past year on Np^{238} by the author in conjunction with H. Slätis and H. Atterling[2] at Nobel Institute of Physics, Stockholm, and in conjunction with T. O Passell and F. Stephens, Jr.[3] at the University of California Radiation Laboratory. The work involves extensive beta spectroscopy in three different spectrometers, spectroscopy of uranium photoelectrons from Np^{238} high-energy gamma rays, NaI scintillation counter work, and various scintillation counter coincidence studies.

The results of the work are summarized in the decay scheme on the next page, which is consistent with the data.

The two intensity figures listed are those calculated on the assumptions that the 146-kev level is fed exclusively by (a) the 925-kev gamma ray, or (b) a hard beta group. It is not possible with the present data to determine the relative amounts of these transitions, although there is evidence for some occurrence of both.

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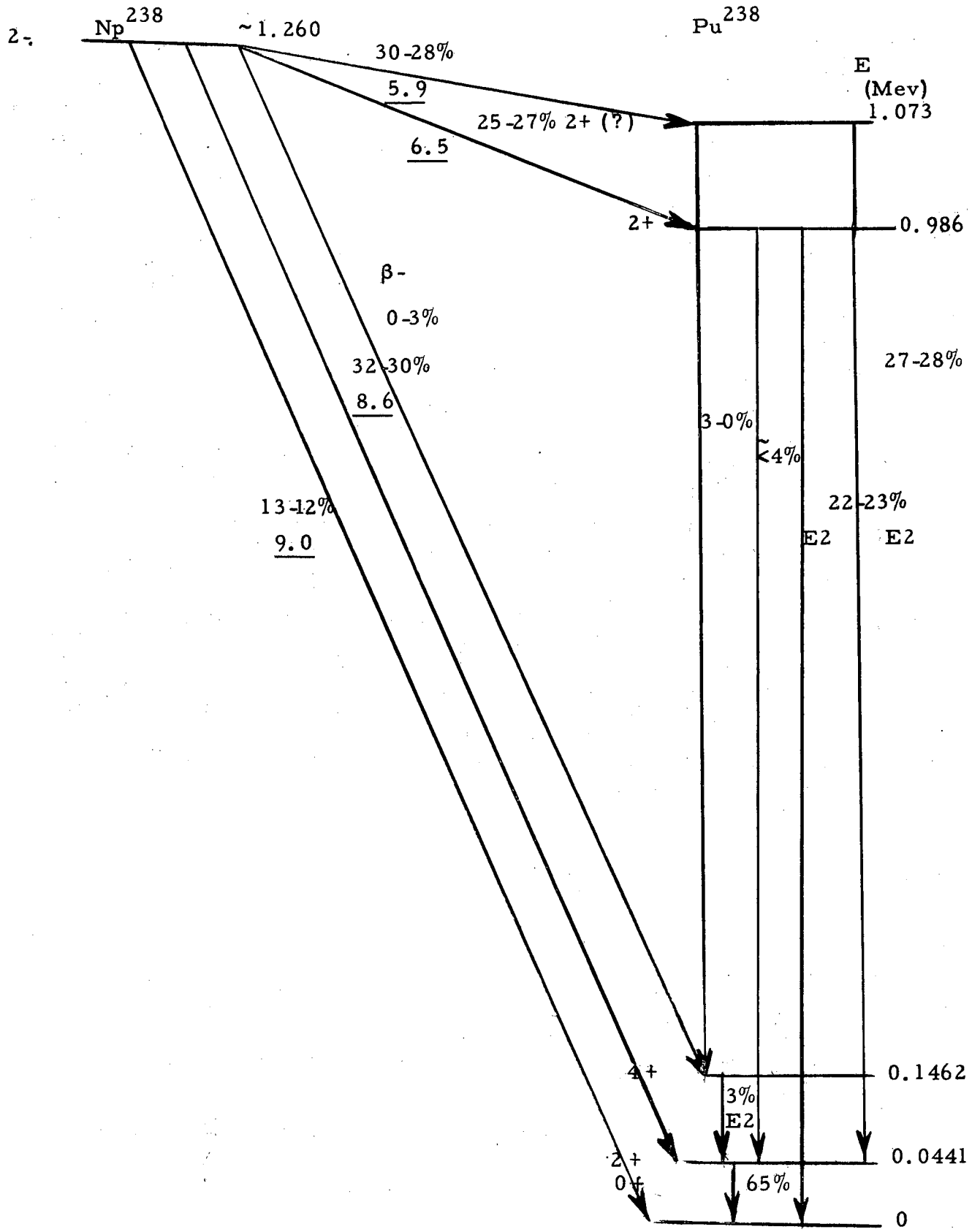
1. M. S. Freedman, A. H. Jaffey, and F. Wagner, Jr., Phys. Rev. 79, 410 (1950).

2. H. Slätis, J. O. Rasmussen, and H. Atterling, Phys. Rev. 93, 646 (1954).

3. J. O. Rasmussen, T. O. Passell, and F. Stephens (to be published).



Log ft values underlined

Table 1 gives the experimental and theoretical[4] K conversion coefficients of the two most intense high-energy gamma rays. The transitions appear to be of E2 nature.

Table I

E_r	Gamma per beta	K conversion electrons per beta	Conversion coefficient (exp.)	Conversion coefficient (theoret.)			
				E1	E2	M1	M2
1.029	0.27	0.0019_9	0.0074	0.0033	0.0102	0.075	0.105
0.986	0.22	0.00204	0.0093	0.0035	0.0108	0.083	0.117

The conversion coefficients of the two weakest high-energy gamma transitions cannot be determined with any accuracy, since the gamma intensities are only indirectly estimated. It does seem that their conversion coefficients are too large to allow E1 assignments.

It is of particular interest to note the log ft value (8.6) for the beta group proceeding to the first excited state, an unusually large log ft value for a $\Delta I = 0$, yes transition. This observation has a simple interpretation in the Bohr-Mottelson strong coupling nuclear model.[5] This model would place a beta transition in the rate group according to ΔI or ΔK, whichever is the greater. In the case of the transition to the first excited state here $\Delta K = 2$. Accordingly, if K were an absolutely good quantum number, the ft values of transitions to ground and first excited states should be nearly the same. The lower ft value of the first excited state transition here could be explained by admixture of about 2% K = 2 character into the predominantly K = 0 first excited state. The similar slower behavior of 2- to 2+ beta transitions for several other examples has been pointed out by King and Peaslee.[6]

4. M. E. Rose, G. H. Goertzel, B. J. Spinrad, J. Harr, and P. Strong, Phys. Rev. 83, 79 (1951).

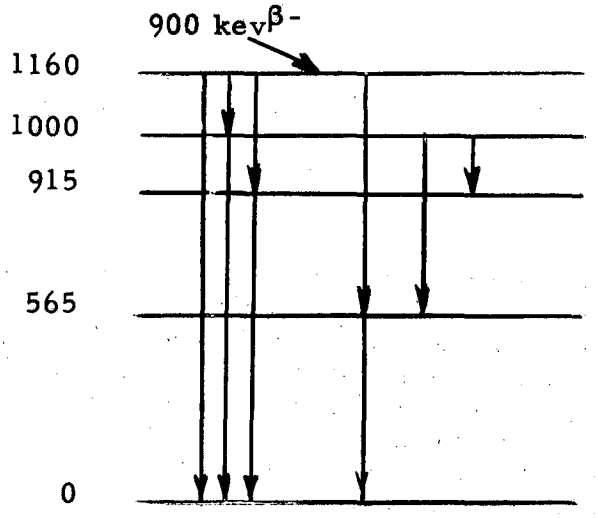
5. A. Bohr and B. R. Mottelson, Kgl. Danske Videnskab. Selskab, Mat-fys. Medd, 27, No. 16 (1953).

6. R. W. King and D. C. Peaslee, Columbia University report CU-132.

NEPTUNIUM-240

Richard M. Lessler

The work on the decay scheme of the 60-min Np^{240} activity previously reported[1] has been continued. Gamma rays of 1160, 1000, 915, 595, 565, and 435 kev have been observed on the NaI crystal scintallation spectrometer, while gamma rays of 245, 160, and 85 kev have been detected by γ-γ coincidence. Gamma-gamma, β-γ and γ-β coincidence measurements have been made with Frank Stephens, and from these results the following decay scheme is indicated:



This coincidence work definitely established the existence of the gamma rays previously in doubt.[1] It also showed a β- of about 900 kev in coincidence with the 1160-kev gamma ray. No other β- was observed in coincidence with the gamma rays. Therefore, the 60-min neptunium is the lower 240 isomer, as its decay energy is about 2060 kev compared to 2156 kev in 7-min neptunium-240.[2]

In an attempt to find Np^{241}, a careful decay curve was run, and no evidence of any activity between the 1-hr Np^{240} activity and the 2.3-day Np^{239} background was found. It is, of course, possible that Np^{241} has a half life of about 1 hr and is masked by the 60-min Np^{240}.

Two 15-minute alpha bombardments of U^{238} foil, followed by fast chemistry, were made to look for a possible short-lived Np^{241} activity. Each time an activity with a half life of about 15 minutes was found in the neptunium fraction. It is possible that this activity is due to fission product contamination. Further work on this 15-minute activity is being done. A positive identification by mass separation of the 60-minute neptunium activity is also planned.

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1. Quarterly Report, University of California Radiation Laboratory Report No. UCRL-2531 (April 1, 1954).

2. J. D. Knight, M. E. Bunker, B. Warren, and J. W. Starner, Phys. Rev. 91, 889 (1953).

THE ALPHA DECAY OF PROTACTINIUM-231

John P. Hummel, Frank Asaro, and I. Perlman

In 1949, Rosenblum, Cotton, and Bouissières[1] reported the following alpha groups in the decay $Pa^{231} \longrightarrow Ac^{227}$.

Particle Energy (Mev)	Abundance	Energy to α (corrected for recoil)
5.042	11%	0
5.002	47%	40
4.938	25%	107
4.838	3%	208
4.720	11%	329
4.660	1-3%	391

Using the alpha-particle spectrograph, we have shown that the group 40 kev from α_0 of 47% intensity is actually two groups having approximately equal intensities and energies 27 and 44 kev less than α_0. (We have succeeded in completely resolving this doublet using a 4 μg thin sample mounted on platinum and masked by an 18-mil slit in the source chamber of the spectrograph). We have also confirmed the existence and approximate energies and abundances of the other groups reported by the French research group. Our experiments also indicate the possibility of a very low-intensity group (about 0.1%) 40 kev lower in energy than the lowest energy group previously reported.

Riou[2] had detected the presence of a 27-kev gamma ray using the selective absorption technique. Since the alpha-decay data of Rosenblum's group showed no place for a gamma ray of that energy, Falk-Vairant and Riou[3] placed a level 27 kev above the ground-state level (which was assumed to be that reached by the highest-energy alpha) and populated it by gamma radiation from higher levels. Our work with the alpha spectrum now shows the existence of a level in fairly high intensity populated by alpha decay 27 kev above the ground state of Ac^{227}.

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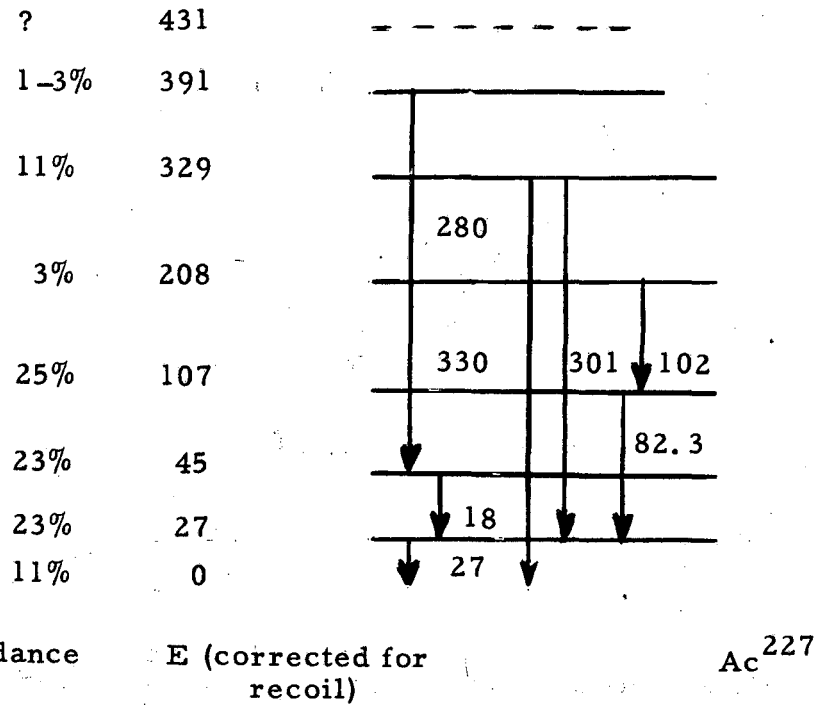
1. S. Rosenblum, E. Cotton, and G. Bouissières, Compt. rend. 229, 825 (1949).

2. M. Riou, Compt. rend. 234, 1157 (1952).

3. P. Falk-Vairant and M. Riou, J. phys. radium 14, 65 (1954).

Using the gamma-ray and conversion-electron data of Falk-Vairant and Riou, the gamma data of Moore,[4] and the alpha-decay data of Rosenblum's group and ourselves, we can suggest the following partial decay scheme:



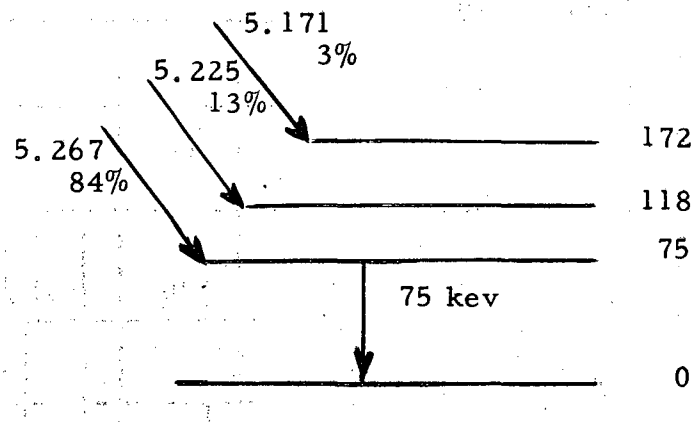
A 383-kev gamma ray has been reported. If the energy of the 1-3% group at 391 kev is in error, the 383-kev gamma ray may fit in deexciting that level to the ground state. This is by no means a complete decay scheme. When it becomes possible to do gamma-ray coincidences with specific alpha groups by using a high-transmission alpha particle spectrograph to resolve the alpha groups, it should be possible to determine decay schemes as complete as this.

4. R. Moore, thesis, Ohio State University, AECU-2757 (1953).

THE LOW-INTENSITY ALPHA GROUPS OF AMERICIUM-243

John P. Hummel, Frank Asaro, and Isadore Perlman

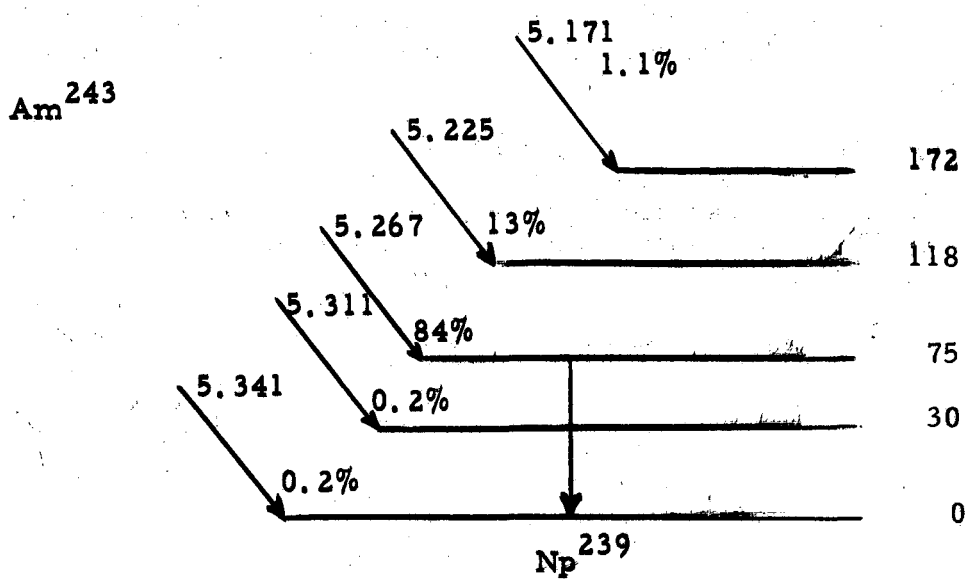
Previous work[1] on the alpha decay of Am^{243} showed three groups of 5.267 (84%), 5.225 (13%) and 5.171 (~3%) Mev energy. Since a very intense 75-kev gamma ray was found in coincidence with most of the alpha particles, the decay scheme suggested was the following:



The ground-state transition was not seen, but was predicted to be of very small abundance (analogous to Am^{241}). Also, another low-intensity group of energy about 30 kev less than the ground-state transition was predicted to be in very small abundance (also analogous to the decay of Am^{241}). In a sample of americium containing over 99% Am^{243} by mass the high energy-low abundance groups were detected with the alpha-particle spectrograph. The energies of these groups are, as predicted, 75 kev and 45 kev higher in energy than the main group. Furthermore, their abundances have been measured and are both 0.2%. Also, a redetermination of the low-energy group of low abundance (reported as about 3%) shows its abundance to be 1.1%. (These calculations were made assuming the 84% abundance of the main group to be correct).

1. F. Asaro and I. Perlman, Phys. Rev. 93, 1423 (1954).

From these data, the following decay scheme is suggested:



It is quickly seen that there is a remarkable similarity between the energy spacings and abundances in the decay of Am^{243} and Am^{241}, the abundances being almost identical.

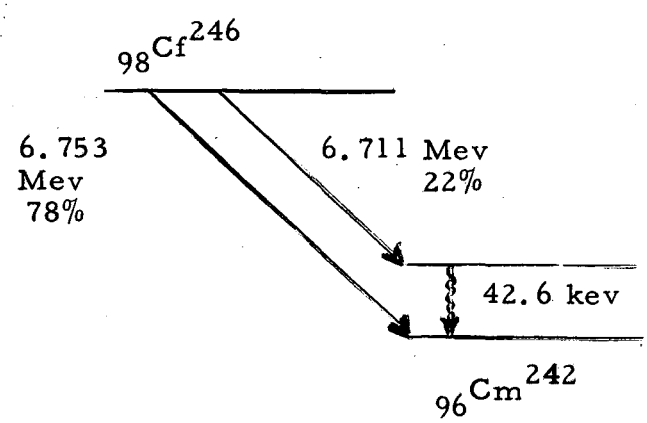
THE ALPHA GROUPS OF CALIFORNIUM-246

John P. Hummel, Alfred Chetham-Strode, Frank Asaro, and Isadore Perlman

Using the alpha-particle stectrograph, we have determined the energies and abundances of the two main alpha groups in the decay $Cf^{246} \longrightarrow Cm^{242}$. The Cf^{246} was produced by alpha-particle bombardment on curium and separated by ion exchange methods. The alpha energy standard used was the 7.127-Mev alpha group of Em^{218}. The energies of the two groups seen are 6.753 ± 0.004 Mev and 6.711 ± 0.004 Mev, and their abundances are 78% and 22% respectively. The main group of Cf^{246} was originally reported by Ghiorso et al.[1] as 6.75 Mev, using an ion chamber measurement. This agrees well with the present determination. Dean Dunlavey, using photographic emulsions to observe α-e^- coincidences, has determined the abundance of the lower-energy group to be 12%. This is not in agreement with our present measurements. However, Frank Stephens calculates a 22% abundance for this group on the basis of his α-L X-ray coincidence experiments.

Correcting for recoil, we find that the energy separation between the two groups becomes 42.6 kev. E. Church[2] reports 42.2 kev for this transition from studies of the decay $Am^{242m} \longrightarrow Cm^{242}$. R. W. Hoff and H. Jaffe similarly report 42.3 kev. Both of these results are in very good agreement with the present work.

The following partial decay scheme results from these measurements.



1. A. Ghiorso, S. G. Thompson, K. Street, and G. T. Seaborg, Phys. Rev. 81, 154 (1951).

2. E. Church, Argonne National Laboratory Classified Report ANL-5141, (November 1953), 0. 6.

THE GAMMA RADIATIONS, AND GAMMA-GAMMA COINCIDENCES IN THE DECAY OF ACTINIUM-226

James Robb Grover

Actinium was prepared by bombarding thorium foil with 340-Mev protons, employing the chemical separation procedure of Hyde.[1] The resulting activity was resolved (using both α- and gross β-γ counting) into 29-hour and 10-day half lives. The activity is believed to have contained only Ac^{225} ($t_{1/2}$ = 10.0 days), Ac^{226} ($t_{1/2}$ = 29 hr), and their associated decay chains.

Since it was desired to obtain the gamma spectrum of Ac^{226} and daughters separately from that of Ac^{225} and daughters, the following device was employed to obtain the spectra for each family alone. The gamma spectrum of the mixture was taken carefully twice, about 2-1/2 days apart, using a sodium iodide (Tl-activated) crystal scintillation counter with a 50-channel pulse analyzer. The analyzer was calibrated against known standards very carefully, until the later energy coverage matched the earlier, channel for channel (within the limits imposed by a small random drift; the counting times were made long enough to average this out). Then, on the assumption that only the two decay groups were present in the gamma spectrum, a pair of simultaneous equations was set up for each of the 50 channels using the two counting rates (taken 61.83 hours apart) for each channel. The resulting pair of spectra looked smooth and continuous, with very little of the staggering of the points around the peaks that one might expect from poor calibration.

The alpha assay was treated in the same manner to give a measure of the Ac^{226} (and daughters) fraction in the sample.

Gamma Rays Observed in the Disintegration of Ac^{226}				
γ-ray energy (kev)	No. of γ-rays per Ac^{226} disintegration	No. of transitions per Ac^{226} disintegration, assuming:		
		E1	M1	E2
~ 47 (?)				
~ 74	medium } prominent peak with two shoulders			
~ 95	large } prominent peak with two shoulders			
~ 115	small } prominent peak with two shoulders			
~ 130 (escape peak) 159	0.34	0.39	3.1	0.92
~ 195 (escape peak) 232	0.53	0.57	2.0	0.76

The intensities of the gamma rays were computed using the α-assay, the known geometry of the counter, and the NaI (Tl) crystal counting efficiencies of Kahn and Lyon.[2] The possible transition probabilities were computed using the K-conversion coefficients of Rose et al.,[3] and the L-conversion coefficients of Gellman et al.[4]

In the Ac^{225} fraction, prominent peaks were seen at 85, 213 and 434 kev, with possible lesser peaks at 120, 152, and 183 kev. This agrees only moderately well with the work of Wagner et al.,[5] who report gamma rays at 165, 230, and 435 kev, and K x-rays.

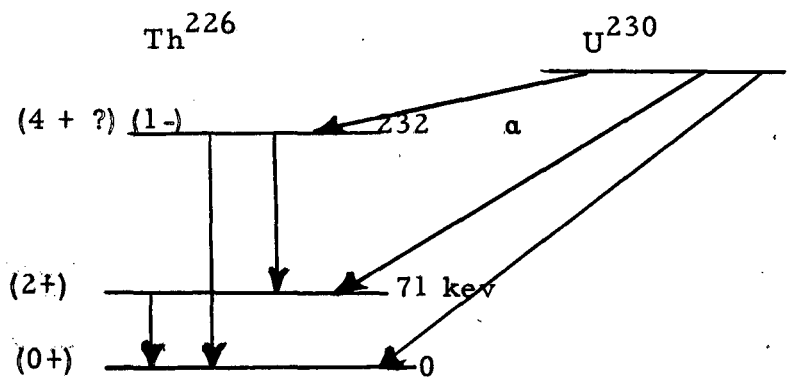
The very prominent 150-and 232-kev gamma rays were shown to belong to the Ac^{226} decay by milking the Th^{226} daughter in order to examine its scintillation gamma spectrum in equilibrium with its daughters. This spectrum agreed with that obtained by Frank Asaro[6] with the Th^{226} daughter from U^{230}, but no gamma rays were found in sufficient abundance to account for the 159-and 232-kev gamma rays. The 115-kev gamma ray corresponds roughly to the 108-kev gamma ray found by Asaro to be the most prominent feature in the Th^{226} equilibrium spectrum.

The gamma-gamma coincidences were done with the help of Frank Stephens. The results were as follows:

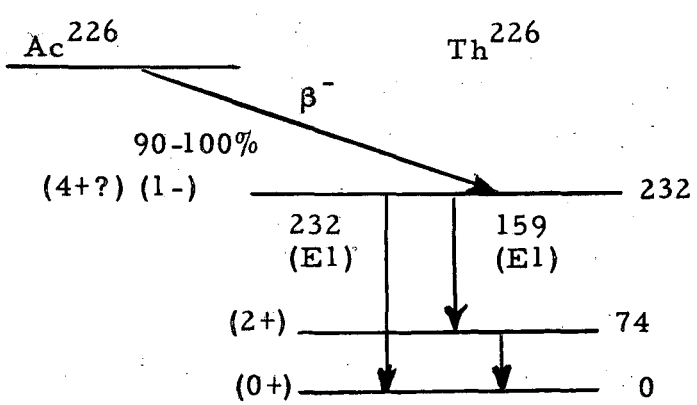
Gamma-gamma Coincidences Found in the Ac^{226}-Ac^{225} Equilibrium Mixture				
γ-rays used to form gating pulse (kev)	γ-rays seen in coincidence with gating pulse (kev)			
L x-rays	K x-rays	159		
70	K x-rays	155		
K x-rays	K x-rays	124	180	248
159	L x-rays	~68	K x-rays	
225 (mixture of 213 and 232)	K x-rays			
180	K x-rays			

Since there are so many different activities in the mixture, two independent equilibrium chains being present, only prominent coincidences are represented here.

Asaro[6] and Stephens deduce the following decay scheme for U^{230} from alpha-decay fine structure and gamma-ray spectroscopy.



All the data gathered in the Ac^{226} decay work are consistent with the same term scheme if the beta decay leads mostly to the 232 kev level in Th^{226}.



From the transition abundance calculations, the 159-and 232-kev gamma rays are most comfortably both E1, although within experimental accuracy other combinations are possible.

At least two things remain to be done with this decay scheme: (1) a beta spectrum should be taken to see if there is more than one beta group, and to get accurate decay energies; (2) the possibility of alpha branching of Ac^{226} should be explored, perhaps by an attempt to milk the Fr^{222} daughter that would result.

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1. W. W. Meinke, Chemical Procedures, University of California Radiation Laboratory Report No. UCRL-432 (1949).

2. B. Kahn and W. S. Lyon, Nucleonics 11, 61 (1953).

3. M. E. Rose, G. H. Goertzel, and C. L. Perry, Oak Ridge National Laboratory Report ORNL-1023 (June 1951).

4. H. Gellman, B. A. Griffith, and J. P. Stanley, Phy. Rev. 85, 944 (1952).

5. F. Wagner, Jr., M. S. Freedman, D. W. Engelkemeir, and L. B. Magnusson, Phys. Rev. 88, 171A (1952).

6. F. Asaro, private communication (1953).

ALPHA DECAY OF SPHEROIDAL NUCLEI

John O. Rasmussen

In a joint program with Dr. Benjamin Segall, work has continued on the theoretical treatment of alpha decay of spheroidal nuclei. The recent work has concentrated on even-even nuclei in a one-body treatment with an inner prolate spheroidal well of constant potential outside which the potential is that produced by a uniformly charged spheroid of the same dimensions as the well. The schrodinger equation in prolate spheroidal coordinates was treated, and coupled second-order differential equations analogous to the radial equations occurring for the problem in spherical polar coordinates were derived.

Numerical integration of the problem for several specific cases is presently being attempted, using the electromechanical differential analyzer at this laboratory.

X-RAY INVESTIGATION OF $CH_3\overset{S}{C}NHNH\overset{S}{C}NH_2$ AND $KF \cdot xHF$

Michael E. Senko

Work is being continued on the determination of the space group of $CH_3\overset{S}{C}NHNH\overset{S}{C}NH_2$ (Methyl thiosemicarbozido dithiocarbonate).

In the investigation of the high-temperature phase of KHF_2 it has been possible to obtain pictures in both thick sealed Pyrex capillaries and in Teflon tubes of interior diameter 0.020 in. and exterior diameter 0.045 in. The results of these pictures have not been conclusive, and work is being continued with new samples.

Work has been started on an investigation of compounds of the form $KF \cdot xHF$.

PRELIMINARY INVESTIGATION OF POTASSIUM HYDROXYLAMINE SULFONATES

Wilbur V. Johnson

Work has been started on the preparation of the potassium hydroxylamine sulfonates and related salts. Potassium hydroxylamine isodisulfonate ($KO_3SONHSO_3K$) has been prepared and a series of oscillation and rotation pictures taken. These data are only exploratory, and a method for growing better single crystals must be found in order to obtain conclusive pictures.

Potassium nitrilosulfonate ($N(SO_3K)_3$) has also been prepared and powder pictures taken. These crystals were too fragile to attempt rotation pictures.

Work is continuing on the preparation and study of these and similar salts.

DETERMINATION OF STRUCTURE OF AURIC CHLORIDE

Edward S. Clark

Work is continuing on the determination of the crystal structure of $AuCl_3$. A large amount of diffraction data has been assembled with Weissenberg patterns for rotation about the a, b, and c axes, and precession patterns with precession about the a and b axes. Careful investigations of these data over the past few months, including the calculation of several Fourier syntheses, have shown that much of these data are not useful. The Fourier projections are not conclusive enough to state parameters with certainty. There are several reasons for this. The gold atom has many electrons and shows strong diffraction. It also exhibits strong absorption effects, and this is a major problem in obtaining useful data. Another problem that has become apparent upon observation of the Fourier syntheses is that good data are required to locate the chlorines accurately, since the chlorine atom has roughly one-fourth the diffracting power of the gold atom.

In light of the above problems, work is being repeated to obtain data of greater accuracy. After microscopic investigations of several crystal preparations in the drybox, a needle crystal of approximately constant cross section was found and carefully sealed in a thin glass capillary for diffraction studies. Weissenberg patterns from this crystal for c-axis (needle axis) rotation seem to exhibit small absorption effects. With copper radiation, Weissenberg patterns for layers hk0 to hk3 have been obtained, and work is in progress in obtaining higher layers beyond the copper wave-length limitation using molybdenum radiation. These photographs will be correlated from precession data on the same crystal. It is not expected that useful intensity data can be obtained for rotation about the a or b axes.

It is hoped that from these new data the accurate structure of auric chloride will be obtained.

BENT-CRYSTAL X-RAY SPECTROMETER

Herman P. Robinson and Alfred A. Wydler

During a run on the X-ray spectrometer, an active sample is moved very slowly around an arc and the X-ray intensity is recorded as a function of position. To facilitate the correlation of sample position with count rate, a photocell and microscope have been fastened to the sample support to view the graduations on the quadrant and make a mark on the count-recording tape whenever a line passes under the microscope objective. The requirements on the amplifier are severe, in that a sweep from one line to the next takes 40 minutes so that the change in illumination on the phototube takes place very slowly, requiring an amplifier of unusually long time constant and high gain. A conventional dc amplifier is ruled out because of fluctuations in average light level. The problem was solved by making a dc amplifier with a gain of about one, and inserting a time constant in the feedback loop. With a positive pulse, corresponding to the signal from a line on the quadrant, the feedback operates with a time constant of about one hour, giving a transient gain of 3000. When the sign of the pulse is reversed, a diode provides a relatively short time constant to reset the base line of the amplifier.

DOUBLE-RETARDING-FIELD ELECTROSTATIC BETA-RAY SPECTROMETER

Herbert R. Johnston

General

The last quarter has been a period of construction and assembly of the DRF beta-ray spectrometer. Approximately 99 percent of the parts have been finished and delivered by the machine shop. Most of the many grid structures required have been completed and delivered. The preliminary assembly of the component parts has been completed.

The new vacuum tank has been checked for leaks, and all leaks have been discovered and eliminated. It has been found that the highest vacuum that may be obtained with the system used is of the order of 3×10^{-6} mm Hg. It is estimated that a vacuum of at least 1×10^{-5} mm Hg is necessary, and it is presumed that this may be obtained without difficulty in the equipment to be used.

Preamplifier

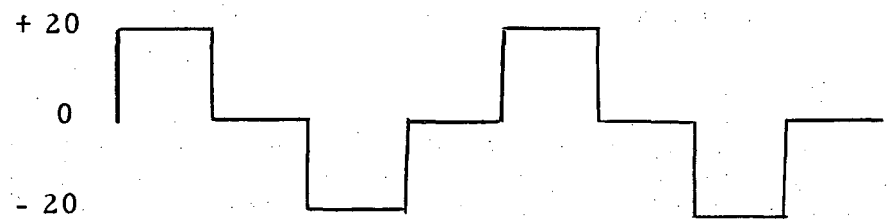
A specially designed preamplifier has been completed and tested. This preamplifier is designed to work from the output of the electron multiplier in the spectrometer into a slightly modified scaler counter (No. 5T1664R). The preamplifier is slightly unusual in that there are four stages of amplification within the negative feedback loop. Some trouble with regeneration and oscillation was successfully eliminated. The final preamplifier uses five 6AK5 tubes, one of which is a cathode follower inside the vacuum tank of the spectrometer. The gain is 40 ± 3 db from 450 cycles to 6.5 megacycles.

NUCLEAR QUADRUPOLE RESONANCE

Gilbert O. Brink

Most of the work done during the last quarter has been the development of the electronic equipment necessary for quadrupole resonance measurements. An oscillator covering the range 3 to 50 megacycles has been constructed and tested. A lock-in detector has also been assembled and tested.

It was originally planned to use frequency modulation to view the lines, but this has been discarded in favor of magnetic field modulation. The field that would be desirable would be of the following shape and would have an amplitude of about 20 gauss.



This wave form is good because the desired signal comes at twice the frequency of the interfering amplitude modulation and can be separated from the am by a suitable filter. One problem in this system is obtaining a reference signal for the lock-in detector that can be varied in phase. A circuit has been designed to do this and will be tested in the near future.

The U^{235} resonance will be difficult to find even though the quadrupole moment is known, because the quadrupole coupling coefficient is not known for any compounds. It may be possible to estimate this coefficient from the known values for other nuclei or from the magnitude of the splitting of the 5f electronic levels in neptunium compounds. Even an order-of-magnitude value of this coefficient might allow a lower limit to be set on the frequencies of the resonance lines. A preliminary calculation has been made but the results were not good enough to allow a lower limit to be set. An attempt will be made to refine these calculations so that they may be useful.

OPTICAL SPECTROSCOPY

John G. Conway and Ralph D. McLaughlin

High-frequency discharge source

A high-frequency electrodeless discharge source with characteristics of 10 megacycles and 25 watts was made by Herman Robinson's group. A source of this type is capable of very high resolution.

In natural Li, in the form of the hydride, the three lines of the hyperfine structure of 6707 Å are well resolved. A Fabry-Perot interferometer crossed with a Wadsworth mount spectrograph is used to photograph the spectra. The LiH is placed in a quartz tube sealed at one end. The tube is evacuated and helium is admitted until a pressure between 3 and 5 mm of Hg is obtained. It seems likely that this method may be applied to the isotopic analysis of lithium.

Neptunium 239

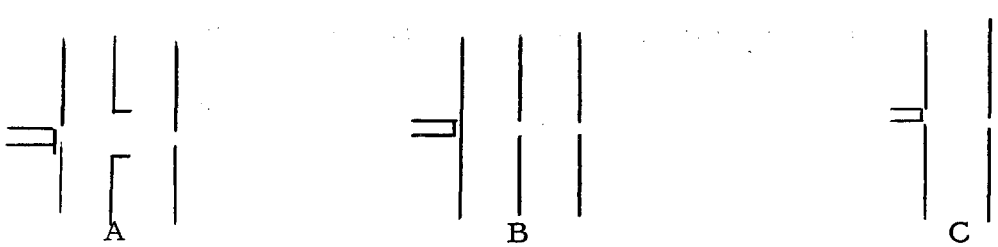
A depleted U^{238} sample was irradiated in the Arco pile to form Np^{239}, which was to be used to determine the nuclear spin and isotope shift of Np^{239}. Although the work on the sample was not satisfactory, it did enable us to obtain a more suitable chemical procedure, which will be used on the next irradiation.

MASS SPECTROSCOPY

F. L. Reynolds

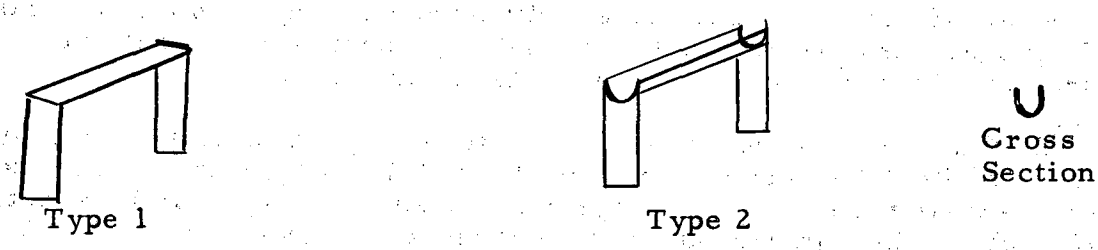
The process of making ions by coating a filament with a salt or oxide of a metal and heating the filament in vacuum under the influence of an electric field corresponds to a complicated phenomenon. In this report a study was made of the efficiency of two different filament shapes used in three source designs. The sample material was Pu^{238}, and the ratio of activity placed on the source filament to that collected on aluminum foil at the receiver was taken as a measure of efficiency. No attempt was made to measure Pu^{+}, PuO^{+}, or PuO_2^{+} beams separately.

Types of source construction:



All slits in above sources are 0.010 in., the total voltage drop in each case is 5 kv, and the intermediate plate is about two-thirds full voltage. The position of the filament is indicated. The final slit is at ground potential.

Filament shape:



Type 1 is a tantalum ribbon filament 0.030 in. wide x 0.001 in. thick, bent as shown. Type 2 is the same filament as above, but bent with the help of a suitable die to have the cross section shown. This cross section is approximately 0.010 in. on a side.

The following results were obtained:

Filament type	Source structure type	Ratio: $\frac{\text{Activity of sample}}{\text{Activity at collector}}$
1	A	1.8×10^7
1	A	3×10^7
1	A	1.4×10^7
1	A	1×10^7
2	A	2×10^5
2	A	4.2×10^5
1	B	1.4×10^7
1	B	2.2×10^7
2	B	3.6×10^5
2	B	2×10^5
1	C	2×10^6
2	C	3.7×10^4

Sample size varied from 0.2 to 0.5 micrograms of Pu^{238}.

From these results it would seem that the U-shaped structure was instrumental in producing more plutonium ions than the flat ribbon structure, regardless of the type of source design. The reason for this result can only be postulated to be (1) the U-shaped filament may retain the sample better upon heating; (2) the U-shaped filament may increase the ionization probability by offering a greater chance for multiple collisions with the hot surface; or (3) there may be a focusing effect owing to the shape of the filament.

GADAC
(ANALOG COMPUTER)

Herman P. Robinson and G. Donald Paxson

This analog computer, which was designed and built to solve such problems as radioactive growth and decay and neutron capture in reactors, is in frequent use for routine calculations of such problems.

A "Hold" circuit is being incorporated to permit changing decay constants during a run. This feature will be useful in solving problems in a reactor where the flux is changed during the bombardment.

SNAPPER PULSE-HEIGHT ANALYZER

Albert Ghiorso and Almon E. Larsh

This report is an expansion of a note in UCRL-1959. Included are some maintenance notes from 18 months' operating experience with this type of analyzer.

A new-type pulse-height analyzer has been designed around the 6BN6 gated-beam tube. The circuits are simple, are noncritical, use few components, and draw low power.

The pulse-height selection is performed by a chain of 6BN6's biased at successively increasing negative voltages on the signal grids. These biases sort the pulses into an integral picture corresponding to an energy spectrum obtained from a radiation detector.

The new and important feature of this system is the use of the 6BN6 as half of a gated univibrator. When the signal pulse exceeds by a few millivolts the bias level of a 6BN6, the univibrator effect takes control and the circuit "snaps" into a pulsed state.

Figure 3 shows the shape of the flat-topped signal pulse fed to the signal grids of the 6BN6's.

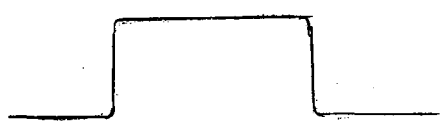


Fig. 3 SIGNAL PULSE, 10 μS

Figure 4 shows the narrow delayed gate pulse, which is provided to allow the flat-topped signal pulse to reach maximum value before the 6BN6's are allowed to operate. The gate pulse is fed to the gate or second control grid of the 6BN6's. Since any pulse-height-selecting device will work better with a pulse whose value is constant during the inspection interval, the use of a gate pulse reduces considerably the uncertainty of selection when a pulse amplitude is near the boundary of a channel.

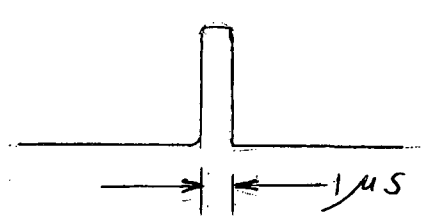


Fig. 4 GATE PULSE, 4μS DELAY, 1μS WIDE

Figures 5 and 6 illustrate the "snap" action of the 6BN6 univibrators. Figure 5 shows the signal voltage at the plate of the 6BN6 when the signal pulse amplitude is not great enough to actuate the channel being observed. Figure 6 shows the superposition of signal pulses on the plate of the 6BN6 when some pulses activate the observed channel while other pulses are not quite of sufficient amplitude to induce univibrator action. It is seen that as a result of snap action the uncertainty of operation of a channel can be eliminated.

Examination of the snapper circuit, the 6BN6$\frac{1}{2}$ 5963 univibrator, will disclose a 51K resistor in the signal grid of the 6BN6. It has been found that a resistor of this order of magnitude is required in the 6BN6 grid to ensure univibrator action. If the impedance which the first grid sees is too low, no snap action will occur, even though positive feedback is still present in the circuit. (See Fig. 9).

Either of the two control grids of a 6BN6 may exercise control of the plate current of the tube during conduction. Since the control action of the grids is about the same, and the grids' cutoff characteristics are sharp, this tube was chosen to act as a pulse-amplitude selector that could easily be gated into operation. The first grid is biased negatively by an appropriate amount to affect pulse-amplitude selection. The second grid is biased negatively to cut off plate current until a signal pulse has reached maximum amplitude. When the gate pulse is applied to the second grid, the tube is free to conduct. If the bias on the first grid has been exceeded by a sufficient amount by the signal pulse, there will be a negative signal fed to the grid of the one half of a 5963. A positive signal will appear on the plate of the 5963. Since the accelerator of the 6BN6 is tied to the plate of the 5963, it will also rise to a higher positive potential, causing the plate current of the 6BN6 to increase, resulting in positive feedback and univibrator or snap action.

For low count rates, the snapper circuit, with an attenuated signal from the plate of the 5963, drives a 30-millisecond univibrator which turns on the register driving tube. A Veeder-Root register register records the event counted in the channel. At the same time that the 30-millisecond univibrator (register univibrator) is triggered, a canceling, or off-turner, pulse is fed from each snapper circuit to the register univibrator of the next lower energy channel to turn it off before it has a chance to fire and actuate the register driving tube. In this manner a differential pulse-height analysis is achieved, since only the highest-energy 6BN6 univibrator to be triggered will actuate the register.

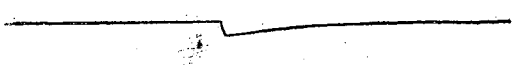


Fig. 5. 6 BN6 PLATE JUST BELOW SNAPPING STATE.

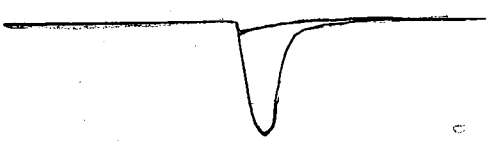


Fig. 6. 6 BN6 PLATE ON EDGE OF SNAPPING. SOME SNAP, SOME DON'T

Figure 7 shows the signal appearing on the cathode of the register univibrator when the grid receives a pulse from its snapper but no off-turner pulse from the channel above. The signal pulse appears on the cathode by cathode-follower action. The triggering of the circuit into univibrator action occurs more slowly because of the time required to charge circuit constants. Only 60% of the plate signal from the snapper is needed to trigger the register univibrator stably.

Fig. 7. REGISTER UNIVIBRATOR BEING FIRED. CATHODE SIGNAL.

Figure 8 shows the cathode signal of the register univibrator when a firing signal is applied to the grid and an off-turner signal is applied to the cathode. The full signal voltage of the snapper is applied to the cathode for off-turner action to assure that the grid of the register univibrator remains negative with respect to the cathode and thus is not actuated.

Fig. 8. REGISTER UNIVIBRATOR CATHODE, SUBJECTED TO OFF-TURNER.

The off-turner signal from a snapper is connected to the cathode of the register univibrator of the channel below through a crystal diode. This is necessary to prevent one register univibrator from triggering the register univibrator of the stage above through part of the 5963 plate load resistor. A high impedance is encountered by signals trying to go in the wrong direction, while off-turner signals are passed with little attenuation.

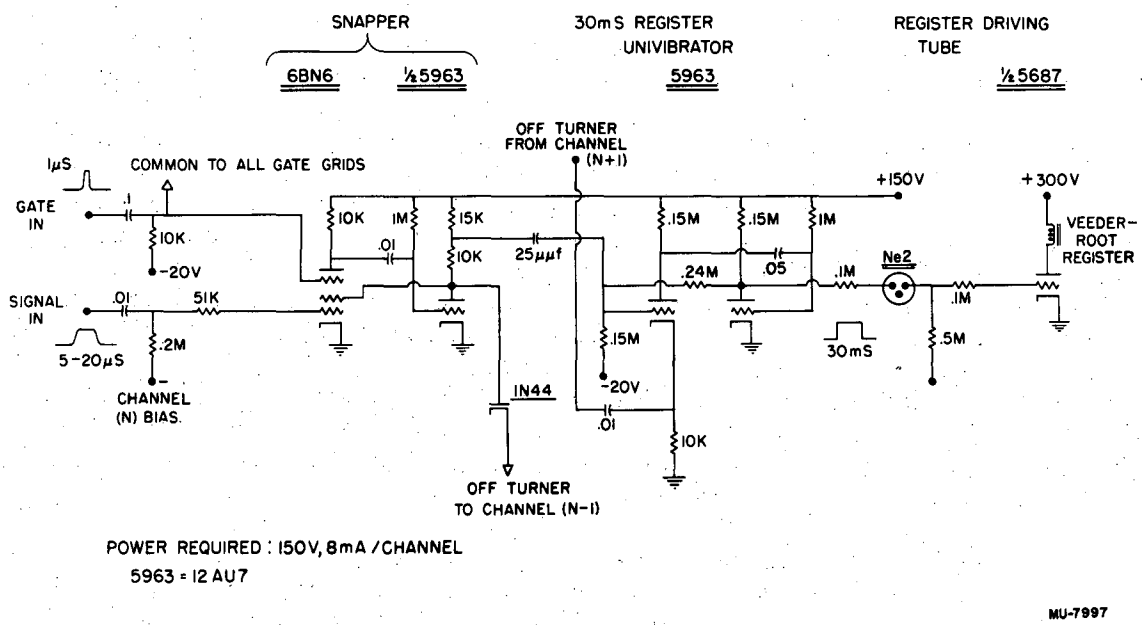

SNAPPER
6BN6
½5963
30mS REGISTER UNIVIBRATOR
5963
REGISTER DRIVING TUBE
½5687
OFF TURNER FROM CHANNEL (N+1)
1μS
COMMON TO ALL GATE GRIDS
GATE IN
.1
10K
-20V
SIGNAL IN
.01
51K
.2M
5-20μS
CHANNEL (N) BIAS
10K
1M
15K
.01
10K
25μμf
1N44
OFF TURNER TO CHANNEL (N-1)
.15M
.15M
1M
.24M
.05
.15M
-20V
.01
10K
+150V
.1M
Ne2
30mS
.5M
.1M
+300V
VEEDER-ROOT REGISTER
POWER REQUIRED : 150V, 8mA /CHANNEL
5963 = 12 AU7
MU-7997

Fig. 9

For count rates high enough to cause an appreciable count loss resulting from the relatively long resolving time of the mechanical registers, a scale of ten may be inserted into any channel by means of a jack on the panel of the pulse-height-selector chassis. When the scaler is plugged into any channel, the register univibrator of that channel becomes a scaler univibrator and has its pulse width shortened from 30 milliseconds to 500 microseconds. A lamp on the register of the scaled channel lights to indicate that the register reading should be multiplied by ten.

Because the circuit of the snapper-type pulse-height analyzer has few components, the construction is very simple. The register univibrator circuit contains the most components and was therefore preassembled on a turret socket. The remaining few components of each channel can easily be tied from the proper socket pin to a signal or voltage bus.

In the design phase of the project, a ten-channel model of the analyzer was constructed. It was easily aligned and retained good short-term stability with a channel width of only ten millivolts. For most work a multichannel of this type will work with a five-volt channel width.

Six 50-channel snapper-type analyzers have been built to date. Two have been running since November 1952 with very little down time for maintenance.

To align a multichannel analyzer, all the channels are switched to the same bias on the signal grid (-5 volts in most cases) and their fine bias adjustment increased to maximum bias. The fine adjustment on the first channel bias is reduced to one-half of its maximum value and a pulse generator signal is fed to the analyzer with just sufficient amplitude to activate the first channel. With the pulse generator left set at this value, the fine bias on the second channel is reduced until that channel is activated and the first channel is turned off. The fine bias on the third channel is then reduced to activate that channel. This procedure is continued until all channels have been adjusted to fire at the same signal level. The range of fine adjustment is sufficiently great that 6BN6's of both high and low sensitivity can be used in the circuits and can be brought into adjustment at the same time.

After all the channels have been aligned at zero channel width, their channel-width biases are switched to 50 mv per channel. The pulse from the pulse generator is then run up and down in amplitude to make sure that all channels fire in proper sequence. If this is the case on the 50-mv channel width, a channel-width error of less than 1% will be assured when the analyzer is run with a channel-width bias of 5 volts.

The use of the 50-mv channel width for periodic alignment checks provides a fast and simple way to check channel boundary-position drifts. If ever any channel doesn't fire in proper sequence on the 50-mv channel-width bias position, one then knows that the channel width of that channel is in error by more than 1%.

On one test a 50-channel analyzer was aligned in the manner described and retained a channel-width stability of better than 1% (50 mv with a 5-volt channel width) during 84 days of continuous operation.

For the most stable operation, any electronic circuit should be operated, as nearly as possible, under constant temperature conditions. In the case of pulse-height analyzers, a constant room temperature is essential for stability of the analyzer and its associated amplifiers. A refrigerating-type air conditioner used in the pulse-analyzer room will not only improve over all amplifier stability, but also will account for lengthened component life.

The snapper, in its present form, has been operated with signal and gate pulse widths both as low as 1 microsecond and a resolving time of 2 microseconds for two pulses not in the same channel. But for normal operation, a signal pulse width of 10 to 20 microseconds is used with a 1-microsecond gate pulse. A long pulse, at least 10 microseconds, is necessary for alpha pulse-height analysis. To keep the entire analyzer as simple to operate and maintain as possible, the input pulse length for scintillation and proportional counters is made comparable to alpha pulse lengths. There is a bias-switching circuit in the 50-channel analyzers to provide channel widths of zero volts for alignment, 50 mv for channel-width stability checks, and 1-, 2-1/2-, and 5-volt operating channel widths to give 250-, 100-, and 50-channel operation.

A simple single-channel analyzer can be made with two snapper circuits and a recorder driving stage. The channel-width bias voltage between the two 6BN6's can be adjusted to the desired value, then the bias on the lower-channel-edge 6BN6 can be varied continuously by a motor-driven potentiometer or can be varied in steps by a switching circuit.

On automatic channel position drive, the snappers could feed through an appropriate off-turner stage into a count-rate meter for recording activity as a function of time and therefore bias level or energy.

In manual operation the snapper could feed through the usual off-turner register univibrator for low count rates, or could actuate a scaler for higher count rates.

For much work, especially on high-count-rate samples and long-half-life activities, a single-channel analyzer will do a sufficiently fast and accurate job of energy analysis. When it is coupled to a recording count-rate meter, a convenient plot of activity versus energy is immediately available for evaluation.

When a low-count-rate sample is to be analyzed or when it is particularly important to record and analyze every event, then a multichannel pulse-height analyzer is needed.

The snapper circuits as shown have been stacked successfully into 50-channel analyzers. Fifty is by no means a limit to the number of channels that can be stacked. It was thought that for the majority of work 50 channels were sufficient for a convenient spectrum spread, so that there would be no loss of resolution on sharp peaks because of too few channels, and yet no large number of excess or unused channels.

In the 50-channel analyzers that have been constructed, the 6BN6 bias switching circuit that has been provided allows for greater flexibility by allowing part of the spectrum to be inspected by all 50 channels.

Since a separate gate pulse, properly delayed with respect to the signal pulse, is required to permit the snapper to operate, a simple method of coincidence pulse-height analysis presents itself. Signals from a second detector, which come in coincidence with the pulses fed to the snapper, can be introduced into the gate circuit of the pulse-height analyzer. Whenever a coincidence occurs, one signal is presented to the snapper for analysis while the other causes gate pulse to be generated that allows the snapper to operate.

For more selective coincidence analysis, the signal from the second detector may first be put through a single-channel snapper before going to the gate circuit to limit the energy range of the second event whose partner is to be analyzed.

Anticoincidence analysis may be performed by supplying the gate-generator circuit in a normal fashion with the pulse to be analyzed, but providing a mixing circuit between the gate-circuit output and the snapper into which a negative gate can be fed from the anticoincidence detector to cancel the regular gate and prevent the signal pulse from being analyzed or recorded.

Such anticoincidence analysis would minimize the escape peaks and Compton smear in scintillation analysis.

In one 50-channel snapper four Veeder-Root registers failed when their driving coils opened up.

Little stoppage has resulted from tube failure. Only one tube, out of a total of 150 tubes, has failed in the last 15 months of continuous operation.

A STUDY OF THE SEALED-TUBE DIGESTION TECHNIQUE FOR THE ANALYSIS OF ORGANIC COMPOUNDS

Charles W. Koch and L. G. Green

The modification by White and Long[1] of the Kjeldahl digestion procedure affords a major improvement to this method of analysis. Subsequently, two investigations[2,3] have shown that conditions of digestion must be carefully controlled or ammonia is not quantitatively recovered from organic samples nor from ammonium sulfate. It was also reported[3] that the type of catalyst added to the digestion mixture may appreciably affect the stability of ammonia at the temperature of the digestion.

The present investigation was undertaken to identify the oxidation product or products of ammonia in the presence of sulfuric acid above 470°C and to establish if possible a set of conditions for the digestion that would result in a less critical temperature control.

The digestion tubes had the dimensions proposed by White and Long.[1] The distillation apparatus employed was described by Kirk.[4] The method deviated from that described by White and Long in that the sulfur dioxide and carbon dioxide formed in the course of the digestion of a sample were driven off by heating the contents of the bomb tube to gentle boiling before transferring to the distillation apparatus. Catalyst was not added to the digestion mixture because of the uncertainty introduced owing to a possible catalytic effect on the decomposition of ammonia. The omission of catalyst also eliminated the need for the addition of sodium thiosulfate to the alkaline distillation mixture in order to reduce the mercuric ion from the catalyst to mercury. The temperature range investigated for the digestion varied from about 450°C to 625°C. The error in furnace temperature readings was less than 5°C.

The experiments of Grunbaum et al.[2] were repeated on a milligram scale. Figure 10, curve A was obtained using bomb tubes with a volume of about 25 ml. Each tube contained approximately 6 mg of ammonium sulfate and 250 μl 18 M H_2SO_4. The samples were heated for 30 minutes in a bomb furnace at the temperature listed. These data are in reasonable agreement with the previously reported work.

It was proposed by Grunbaum et al. that the ammonia loss probably was due to oxidation of ammonia to nitrogen gas. To confirm that this process was the one which was occurring, 6 mg of ammonium sulfate and 250 μl of 18 M H_2SO_4 were sealed in a 25-ml bomb tube under vacuum (10^{-4} mm), and the contents were digested under conditions in which the ammonia was quantitatively lost (624°C for 30 minutes). The composition of the gas phase was determined by use of the mass spectrograph. Within the accuracy of the analysis it was found that the ammonia was oxidized quantitatively to nitrogen gas (gas recovery = 105%). Oxygen gas also was present in the gas mixture after digestion. Its presence is due to the decomposition of sulfur trioxide at the temperature of digestion.

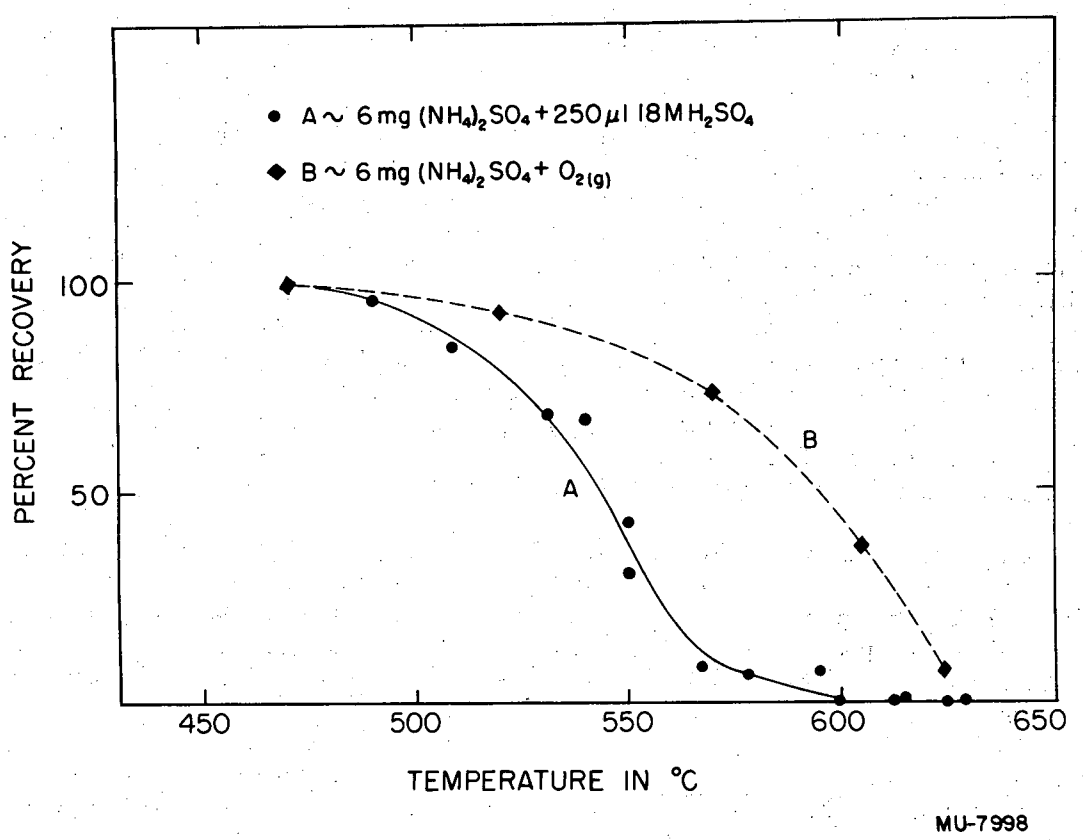


Fig. 10 Effect of temperature on the oxidation of $(NH_4)_2SO_4$ in concentrated sulfuric acid and in air.

Because the pressure of oxygen gas over the temperature range investigated is appreciable, it was of interest to compare the decomposition of ammonia by oxygen with that by sulfuric acid. Curve B of Fig. 10 shows the results of such experiments. It is seen that the oxidation of ammonia occurs in approximately the same temperature region, but at a slower rate in pure oxygen than in sulfuric acid. The fact that oxidation of ammonia starts at approximately the same temperature in the presence of oxygen as when the sample is digested with sulfuric acid would seem to afford evidence that oxygen is responsible for the ammonia loss.

It was proposed previously[2] that at the end of a half-hour digestion period further oxidation of ammonia would not occur at a given temperature. Baker[3] corroborated this belief using organic samples at 420° and 465° C in the presence of a mercury-selenium catalyst. Several experiments performed in the present study at higher temperatures, where the oxidation occurs at a more rapid rate, show that equilibrium is not attained in such a short time interval. Table II shows two sets of data: one set in which the sample and acid were sealed in the presence of air and a second in which the tube was evacuated before sealing.

Table II

Variation in Ammonia Loss with Time Using 6 mg $(NH_4)_2SO_4$

Composition of Digest	Temp °C	Digestion Time	%NH_3 lost
In Air			
250 µl H_2SO_4	550	0.5 hr	57, 69
250 µl H_2SO_4	550	1.0 hr	85
In Vacuum			
100 µl H_2SO_4	620	0.5 hr	63
100 µl H_2SO_4	620	1.0 hr	87

From these data it is seen that approximately the same fraction of ammonia is lost in the second half-hour interval as in the first interval. Therefore, equilibrium conditions are not attained in the digestion of the sample and prolonged heating enhances the loss of ammonia due to oxidation.

Initial experiments in which distilled water was added to the sulfuric acid digestion mixture indicated that the presence of water suppressed the rate of ammonia loss. Figure 11 shows the effect of water on the decomposition of tryptophane at 550° C. This temperature was selected because ammonia is rapidly oxidized in the presence of sulfuric acid and the effect of water can be shown using digestion periods of short duration. Curve A indicates the rate of decomposition when 250 μl of 18 M H_2SO_4 are used to digest a sample of tryptophane, and Curve B illustrates the decomposition rate when 250 μl of 18 M H_2SO_4 and 250 μl of distilled water are used for the digestion. It is seen that the organic material is destroyed in less than 10 minutes in both cases, but that the rate of oxidation of ammonia is decreased considerably by the increased pressure of water vapor (total pressure approximately 30 atm). The addition of water to the digestion mixture, therefore, very markedly reduces ammonia oxidation and permits a less critical control of temperature for the digestion. Similar experiments at 530° C showed that tryptophane could be heated for 30 minutes and the ammonia recovery was equal to or greater than 99%. Likewise, under these conditions a 10-minute digestion period was adequate to oxidize the organic portion of the sample. This effect of water probably is due to the suppression of the sulfur trioxide concentration, which in turn will reduce the amount of oxygen gas formed at a given temperature.

The digestion procedure in sealed tubes used for this investigation furnishes the interesting possibility that several elements in one compound could be determined from one sample digestion if the gases in the sealed tube could be collected quantitatively. Preliminary experiments have indicated that the procedure is a practical one. The apparatus used for these analyses is shown in Fig. 12. The two compounds analyzed were acetanilide and chloroacetanilide.

The organic samples, together with 250 μl of sulfuric acid and 25μl of water, were sealed in bomb tubes which had been swept with nitrogen gas and which were drawn to fine tips so that they could be opened easily. Before the bombs were attached to the apparatus shown in Fig. 12, the samples were digested in a furnace at 490°C. After the bomb had cooled the sulfuric acid was expelled from the tip and upper portion of the bomb by heating. When the bomb had again cooled, the capillary was scratched with a file to facilitate its opening later. The bomb was attached to the apparatus by means of a piece of tygon tubing and the position of the capillary was adjusted so that it could be broken by the plunger after the assembly was evacuated. The first absorber contained neutral 5% H_2O_2 and the second one 0.1 M NaOH. With stopcock A closed, the system was evacuated though C. After the system had been evacuated, stopcocks B and C were closed, the capillary was broken, stopcock B was opened carefully and the gas allowed to flow through the two absorbers. When the flow rate through B had slowed sufficiently, the system again was evacuated through C. Following evacuation, stopcock A was adjusted to maintain a slow rate of gas flow through the absorbers and the bomb tube was heated to expel the gases that had been contained in the bomb. The transfer of these gases was aided by slowly distilling water that had been added to the bomb initially from the tube into the nitrogen gas stream.

After the transfer of gases had been effected, the solutions in the absorbers were transferred to Erlenmeyers. To the solution containing carbonate in excess, 2 ml of 1.3 M $BaCl_2$ were added and the excess base was back-titrated to a phenolphthalein end point with 0.1 M HCl. The H_2O_2 solution, which had absorbed the sulfur dioxide and HCl if it were present, was titrated with 0.1 M base to a phenolphthalein end point. It was necessary to remove oxygen from the bomb tube before it was sealed and from the absorbing apparatus before the bomb was opened. In both cases, sulfur dioxide would react with oxygen to form sulfur trioxide.

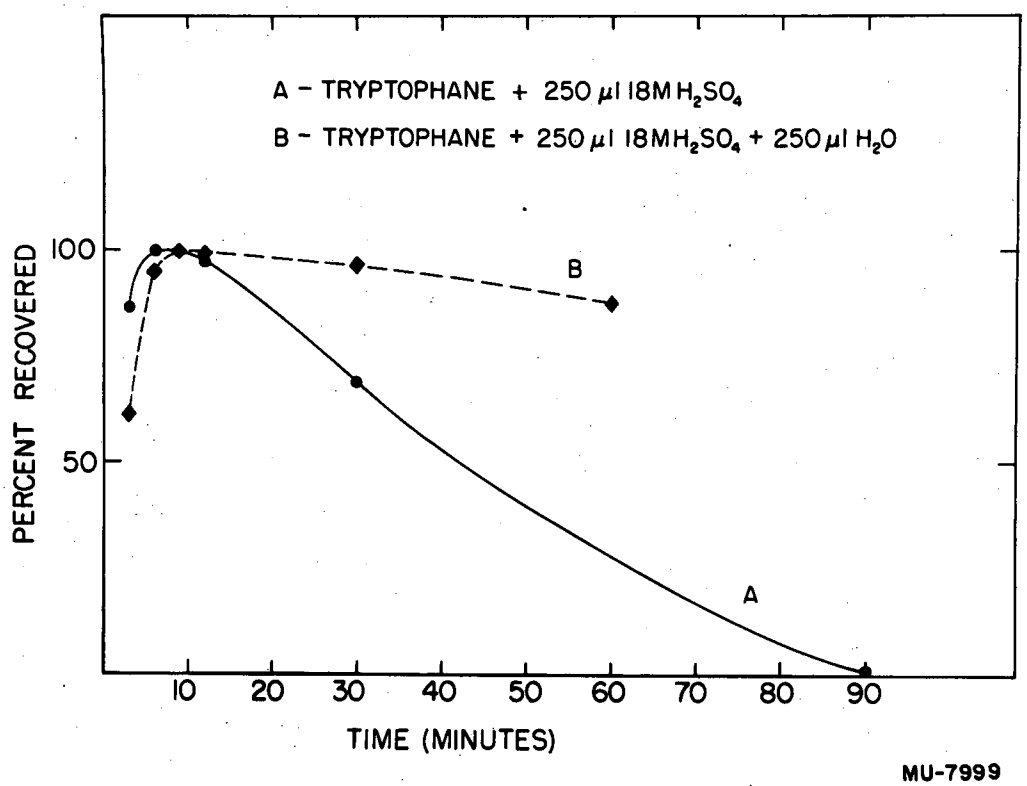


Fig. 11 Effect of water on the oxidation of the ammonia nitrogen in tryptophane at 550°C. Digestion time 0.5 hr.

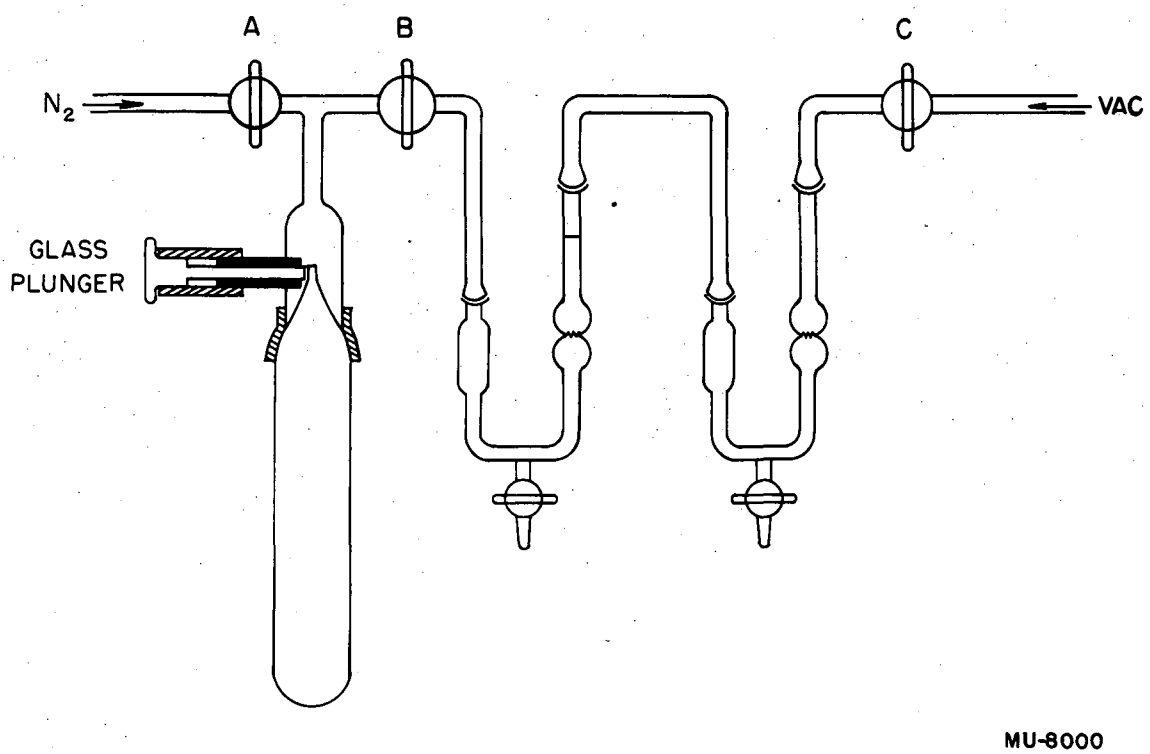


Fig. 12 Apparatus for separating ammonia nitrogen, carbon dioxide, sulfur dioxide, and/or hydrogen chloride.

The reaction for the oxidation of acetanilide with sulfur trioxide may be written:

$$C_6H_5NHCOCH_3 + H^+ + 18SO_3 = 8CO_2 + NH_4^+ + 3H_2O + 18SO_2.$$

For the oxidation of chloroacetanilide the equation is:

$$ClC_6H_4NHCOCH_3 + H^+ + 17SO_3 = 8CO_2\ NH_4^+ + HCl + 17SO_2 + 2H_2O.$$

Table III lists some data obtained for these two compounds using the Kjeldahl method for the determination of ammonia nitrogen in addition to the method described herein.

Table III

Recovery of Gases from Digestion of Two Organic Compounds

Sample	Moles CO_2 / moles of sample		Moles NH_3^+ / moles of sample		Moles H^+ formed / moles of sample	
	theor.	found	theor.	found	theor.	found
Acetanilide	8	8.00	1	1.000	36	35.0
		8.02		0.984		35.9
		8.01		0.984		35.8
		8.04		0.991		35.0
Chloroacetanilide	8	8.00	1	0.996	35	35.0
		8.05		0.989		35.0

In the chloroacetanilide results, 35 moles of H^+/mole of sample represents total recovery of the HCl as well as of the SO_2. To date the solution has not been analyzed for the chloride content directly.

On the basis of these preliminary results, the investigation is being extended.

1. L. M. White and M. C. Long, Anal. Chem. 23, 363 (1951).
2. B. W. Grunbaum, F. L. Schaffer, and P. L. Kirk, ibid., 24, 1487 (1952).
3. P. R. W. Baker, The Analyst 78, 500 (1953).
4. P. L. Kirk, Ind. Eng. Chem., Anal. Ed. 8, 223 (1936).

CHEMICAL ENGINEERING (PROCESS CHEMISTRY)

NOTES ON EXPERIMENTS IN PROGRESS

Preparation of Titanium Metal — Alfred W. Peterson, LeRoy A. Bromley

The results of this work are being published in UCRL-2523.

Thermal Diffusion in Liquids — John E. Powers, Charles R. Wilke

This work has been completed and will be reported shortly.

Capacity of Perforated-Plate Liquid-Vapor Contacting Columns. — C. D. Hunt, Donald N. Hanson and Charles R. Wilke

This work has been completed and will be reported shortly.

Gas-Phase Mass Transfer Studies. — Edward J. Lynch, Loren Hov and Charles R. Wilke

Experiments have been performed in the packed-bed apparatus on the drying of nitrobenzene from porous pellets. Air, helium, hydrogen and carbon dioxide have been used as the drying gases. The carbon dioxide data scattered badly as a result of absorption in the nitrobenzene. Data for the other three gases correlated very well on a plot of HTU vs. ρu^2, with the Schmidt number entering to the 0.37 power. Since the group ρu^2 has the units of force per unit area, changes are now being made in the equipment to check the effect of forces of elasticity.

Psychrometric studies are continuing, using calibrated thermometers for the wet and dry bulbs. The exposed stems have been covered by glass jackets containing air at the thermometer temperature. This eliminates the need for stem corrections. The results with this system are in good agreement with the theoretical curve. No explanation has been found as yet for the variations experienced in the runs using thermocouples.

Vacuum Flow through Annular Sections — Walter Dong, LeRoy A. Bromley

Parts of the equipment for the experiment on vacuum flow between parallel plates were received from the shops and the equipment was set up. However, because the 1/8 in. diam. "O" rings were slightly undersized a good seal was not possible. A 1/8-in. x 1/8-in. square ring was tried, but this was too big, as the rubber stock actually measures more than 1/8-in. x 1/8-in. We will try to form a seal by removing a strip from this square ring. Otherwise, we are ready to take experimental data.

Agitation of Liquid-Liquid System — J. Leonard Fick and Theodore Vermeulen.

The results of this work are being published in UCRL-2545.

Thermal Conductivity of Gases at High Temperatures

Stephen Whitaker and LeRoy A. Bromley

The second attempt to obtain usable vacuum-cast silver failed, and this line of attack has been dropped. Negotiations are now under way with a firm to supply silver with the desired high-temperature characteristics.

The casing for the thermal-conductivity cell has been satisfactorily assembled, and the final assembly of the casing and the solid copper block will be accomplished as soon as two slight modifications on the block have been completed.

The furnace supports have been changed slightly to permit the final assembly.

GENERAL CHEMISTRY

W. M. Latimer, Director

METALS AND HIGH-TEMPERATURE THERMODYNAMICS

Leo Brewer, Richard Brewer, John Engelke, William Hicks, James Kane, Oscar Krikorian, and Ketil Motzfeldt

Determination of Ground States of Gaseous Molecules

Experiments are under way to attempt to determine the ground state of the SO molecule by absorption experiments. Equipment is complete for the determination of the ground state of C_2 by emission experiments.

Vaporization and Condensation Coefficients of Molecular Beams

All metals tried -- including intermediate elements like bismuth, germanium, and silicon -- appear to have unit vaporization and condensation coefficients except possibly for Cr, which does show small but detectable reflection. Arsenic has a very low vaporization coefficient, probably below 10^{-3}, and also a low vaporization coefficient. By analogy with phosphorous, it is expected that this is due to vaporization of As_2 molecules, even though As_4 is the predominate species. However, the literature indicates that As_4 is the main species in Langmuir-type experiments. It is hoped that this can be checked with a mass spectrometer.

Gaseous Carbon Species

Experiments designed to fix the formula of the molecule responsible for the strong ultraviolet continuum in stars and other carbon systems have been repeated with higher accuracy, and have established the molecule to be C_3. Experiments to fix the heat of sublimation are in progress. Vapor pressures of metallic carbides are being checked for indication of carbon species with low accommodation coefficients.

King Furnace Testing

The new King furnace that is to be used for determination of absolute absorption coefficients and heats of formation of high-temperature molecules is being tested for uniformity of temperature and accuracy measurements.

Study of Vapor Species

Na_2CO_3 and molybdenum chloride are being studied, using Knudsen and flow methods, for determination of the important chemical species in the vapors.

Refractory Silicides

The work is completed and has been summarized in UCRL-2544.

Papers for Publication

A paper summarizing work on SiO has been published in J. Phys. Chem.

A paper summarizing work on MgO has been accepted by J. Chem. Phys.

BASIC CHEMISTRY, INCLUDING METAL CHELATES

Howard Cady, Robert E. Connick, Armine Paul,
Richard Poulson, and Robert Wood

Results of Recent Fluoride-Complexing Experiments

The fluoride complexing of Ag^{+}, Hg_2^{++}, Hg^{++}, and Sn^{++} has been studied at 25°C by emf methods.

The silver was studied using a concentration cell containing $Ag-Ag^{+}$ electrodes. The equilibrium constant for the formation of the silver fluoride complex determined by this method agrees with the value in the literature within 10%.

The fluoride complexing of Hg_2^{++} was studied by means of a concentration cell, each half of which contained the $Hg-Hg_2^{++}$ couple. The complexing of Hg_2^{++} by fluoride ion was found to be negligible.

The complexing of Hg^{++} was studied using a cell, one half of which contained the $Hg-Hg_2^{++}$ couple and the other half an $Hg_2^{++}-Hg^{++}$ couple. The fluoride complex of Hg^{++} was found to be somewhat more stable than that of other dipositive ions of similar radius.

The fluoride complexing of Sn^{++} was studied by means of a concentration cell containing Sn amalgam - Sn^{++} electrodes, using essentially the method of Vanderzee. The data have not yet been completely interpreted. However, it can be said that a series of fluoride complexes form, containing one, two, and three fluoride ions per stannous ion. The first fluoride complex is extremely stable - approximately several thousand times more stable than that of other dipositive ions.

Chemistry of Ruthenium

During this quarter attempts have been made to make pure Ru_{IV} and Ru_{III} chemically from RuO_4. The requirements of the reactions are: no interfering spectra caused by the reducing agent, no complex-ion formation, and formation of a pure species.

The most satisfactory method of making Ru_{IV} is reduction of the RuO_4 (excess) with Hg_2^{++} followed by extraction of the excess RuO_4 with hexane.

Chemistry of Titanium (II) Ion

Titanium (II) iodide has been prepared here by the method of J. D. Fast involving reduction of titanium (IV) iodide by metallic titanium. The yield was low, but of satisfactory purity. An attempt is being made to improve the yield.