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NUCLEAR CHEMISTRY

G. T. Seaborg and I. Perlman

THEORY OF ALPHA DECAY OF SPHEROIDAL NUCLEI

John O. Rasmussen

A theoretical study of the alpha decay process for spheroidal nuclei is being carried out. The nuclear models of Bohr and Mottelson[2] and of Hill and Wheeler[3] both predict considerable spheroidal deformations for nuclei of even-even as well as odd types, especially in regions much removed from nucleon closed shells.

First, the effect of nuclear radiation fields in coupling different alpha decay groups outside the nucleus is considered. The E2 transitions between ground and first excited states of even-even nuclei have generally been found to be extraordinarily fast; hence, the coupling effects should be relatively greatest in even-even nuclei. Wave equations governing alpha decay with electric quadrupole coupling are derived using Bohr–Mottelson strong-coupling nuclear wave functions.

Second, it is shown that a simplifying transformation of angular variables may be made for alpha decay of a spin-zero nucleus. This transformation might be called a "center of moment" transformation in analogy to the familiar center-of-mass transformation. The angular variables entering into the wave equation are thus reduced from four to a single variable. The amplitudes of the various alpha wave groups at any fixed distance are just the Fourier components of the alpha wave function in the angular variable.

Experimental data from alpha spectroscopy are examined to determine probable relative wave group amplitudes very near the nucleus. Their significance as Fourier components is considered.

A possible reason for the general decrease of alpha decay rate to the 4+ state as one goes to the heaviest isotopes is discussed.

The dependence of alpha decay rates of even-even nuclides upon decay energy and atomic number has been remarkably well explained by coulombic barrier penetration treatments.[1] Some of these treatments have differed widely in their specific assumptions about the "lifetime in the absence of a barrier," but by the choice of somewhat different values for the nuclear radius in the various cases good agreement with experimental decay rates of even-even nuclides is secured.*

The nucleus is generally assumed to have a spherically symmetric distribution of charge. The nuclear model of A. Bohr and B. R. Mottelson,[2] however, attributes large spheroidal distortions to nuclei lying in regions

*The nuclides Po^{210}, Po^{208}, and Em^{212} are exceptions, decaying more slowly by factors of 5 to 20. They have 126 or fewer neutrons.

much removed from closed neutron or proton shells. Such distortions can be present for even-even nuclei and give rise to an intrinsic electric quadrupole moment, Q_o.

One effect of introducing spheroidal distortion is to bring some nuclear matter out to greater radial distances. Hill and Wheeler[3] have suggested that the above effect might lead to increased alpha decay rates by virtue of a thinner potential barrier, and they estimate this effect by calculating the one-dimensional penetration factor through the thinnest part of the barrier. An important fact to realize, though, is that if such "directed" alpha emission takes place, it necessarily implies the presence of a mixture of different angular momentum waves of alpha emission.* Furthermore, the relative amounts of various angular momentum components may change with radial distance through the coupling influence of the intrinsic electric quadrupole moment of the daughter nucleus. The influence of such noncentral electric interactions between the nucleus and alpha-particle has been treated theoretically by Preston,[4] and the treatment of coupling in this paper parallels his in many important respects.

Even-even nuclides of the heaviest elements ($Z \geqslant 88$) are observed[5] generally to decay by alpha emission to ground and excited states that are interpreted by the unified nuclear model as members of a rotational[6] band sequence with even parities, spins of 0, 2, 4, . . ., and energies $(\hbar^2/2\zeta)I(I + 1)$. (Here $(\hbar^2/2\zeta)$ = the rotational quantum energy.) The different angular momentum states of the outgoing alpha-particle wave necessary for a description in terms of directed emission involve the above states of the nucleus.

In order to gain from experimental alpha-decay rate data a real understanding of the fundamental nature of the process, it is necessary first to solve the well-defined quantum mechanical problem of the outgoing waves in the region beyond the range of short-range nuclear forces. The separate application of simple barrier-penetration formulas to the various alpha groups may give misleading information as to the true magnitudes of the wave functions near the nuclear radius. Preston[7] has stated the problem clearly. One might assume reasonable values for the various alpha groups near the nucleus, integrate the wave equation outwards to large distances, and compare the magnitudes of the various outgoing waves with the experimental intensities. Preston states that small errors in the initial boundary conditions or in the integration might lead to the spurious appearance of considerable amounts of incoming waves at infinity and thus invalidate the results. Preston chooses, rather, to let the experimental intensities of the N alpha groups provide N restrictive boundary conditions on the waves at large distances, and integrates inward toward the nucleus. The phases of the N waves must be chosen so as to satisfy boundary conditions at the nuclear surface.

Quadrupole Coupling of Alpha Decay Groups

The complete Schrödinger equation for alpha decay is set up and the following set of coupled radial equations derived.

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*The author is indebted to Dr. Ben R. Mottelson for pointing this out.

$$\frac{d^2 w_L}{dr^2} - \left[\frac{2m}{\hbar^2}\left(\frac{2Ze^2}{r} - E\right) + \left(\frac{m}{\zeta} + \frac{1}{r^2}\right) L(L+1)\right] w_L$$

$$= \frac{2mQe^2}{\hbar^2 r^3} \sum_{\substack{j=0 \\ j \text{ even}}}^{\infty} w_j (LL00 \mid P_2(\cos\omega) \mid jj00),$$

where

r is the separation distance between nucleus and alpha,
m is the reduced mass,
Z is the charge of the daughter nucleus,
Q is the intrinsic quadrupole moment of the daughter nucleus,
e is the electrostatic unit charge
E is the total alpha disintegration energy,
ζ is the nuclear rotational moment of inertia,
$(LL00 \mid P_2(\cos\omega) \mid jj00)$ are Racah coefficients.[7]

From Racah's general formula[7] we can determine that the coefficients vanish here if L and j differ by more than 2 or if L and j are both zero. For the nonvanishing coefficients we derive the following general expressions:

$$(\mu\mu 00 \mid P_2(\cos\omega) \mid \mu\mu 00) = \frac{\mu(\mu+1)}{(2\mu+3)(2\mu-1)}$$

$$(\nu\nu 00 \mid P_2(\cos\omega) \mid \nu+2,\ \nu+2 00) = \frac{3(\nu+2)(\nu+1)}{2(2\nu+3)(2\nu+5)^{1/2}(2\nu+1)^{1/2}}.$$

It is shown that these particular Racah coefficients are simply related to Clebsch-Gordan coefficients as follows (notation is that of Blatt and Weisskopf[8]):

$$(LL00 \mid P_2(\cos\omega) \mid jj00) = \frac{(2L+1)^{1/2}(2j+1)^{1/2}}{5} C_{Lj}(20;00)^2.$$

Further, it is shown that they are related in the following way to integrals over triple products of Legendre polynomials, a general formula for which has been given by Racah:[8]

$$(LL00) \mid P_2(\cos\omega) \mid jj00) = \frac{(2L+1)^{1/2}(2j+1)^{1/2}}{2} \int_0^{\pi} P_L(\cos\omega) P_2(\cos\omega) P_j(\cos\omega) \sin\omega d\omega.$$

Preston[4] has given a perturbation treatment to solve systems of coupled equations like the above ones. However, estimates of the magnitude of coupling in the case of nuclei near Cm^{242} show that Preston's treatment is not applicable. Some numerical studies of the behavior of solutions of the coupled equations is contemplated using the differential analyzer of the UCRL theoretical group.

Fourier Interpretation of Experimental Data

Until the effect of coupling on the alpha group ratios can be evaluated, we must confine our tentative discussions to values based on simple penetration formulas neglecting coupling. Taking the experimentally determined relative intensities of alpha groups to 0+ (ground), 2+, and 4+ states of even nuclei, we calculated the ratios of wave amplitudes near the nucleus ($r = 1.1 \times 10^{-12}$ cm), taking into account the differences in penetration factor from differences in energies and from the centrifugal potential. Table I lists these values.

It is to be noted that the $|w_2| : |w_o|$ ratio decreases slightly with Z, and the $|w_4| : |w_3|$ ratio decreases rapidly. There is some erratic variation along with the trends. It is suggested that the trends are a result of the increasing intrinsic quadrupole moment. The moment would affect the ratios both through external coupling and through systematic alteration of the form of the angular wave function at the nuclear radius. The last column in the table gives a parameter which should be proportional to the intrinsic quadrupole moment, namely the atomic number (daughter nucleus) divided by the square root of the energy of the first excited state. It should be pointed out that the two effects mentioned for decreasing the apparent $|w_4| : |w_o|$ ratio would with greater distortion presumably bring w_4 to zero and then increase it (in the opposite sign). The zero point may occur for values of the parameter of the order of 14.5 to 15.

The erratic variations in the ratios might indicate that there are specific effects depending on the configurations of the most lightly bound neutron and proton pairs.

The treatment lends itself directly to the analysis of decay of odd nuclear types also, although the cases will in general be more complicated.

Study is continuing along these lines.

Table I

Apparent Relative Wave Amplitudes
at 1.1×10^{-12} cm
(neglecting quadrupole coupling effects)

Alpha Emitter	$\lvert w_2 \rvert : \lvert w_o \rvert$	$\lvert w_4 \rvert : \lvert w_o \rvert$	$Zd/E_2^{1/2}$
Ra^{224}	1.2	--	5.53
Ra^{226}	1.4	--	6.27
Th^{226}	1.2	1.8	8.14
Th^{228}	1.3	0.64	9.56
Th^{230}	1.2	(1.4)	10.7
Th^{232}	1.2	--	11.9
U^{230}	1.1	0.7	10.8
U^{232}	1.2	0.5	11.8
U^{234}	1.1	(0.7)	13.1
U^{236}	1.2	--	12.7
U^{238}	1.1	--	13.4
Pu^{234}	0.7	--	13.4
Pu^{236}	0.8	--	13.7
Pu^{238}	1.0	0.22	13.7
Pu^{240}	1.0	0.25	13.9
Cm^{242}	1.0	0.11	14.2
Cm^{244}	1.0	--	14.3
Cf^{246}	0.6	--	14.6

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   J. J. Devaney, Phys. Rev. 91, 587 (1953).
2. A. Bohr and B. R. Mottelson, Dan. Mat. Fys. Medd. 27, No. 16 (1953).
3. D. L. Hill and J. A. Wheeler, Phys. Rev. 89, 1133 (1953).
4. M. A. Preston, Phys. Rev. 75, 90 (1949).
5. J. M. Hollander, I. Perlman, and G. T. Seaborg, Revs. Modern Phys. 25, 469 (1953).
6. A. Bohr and B. R. Mottelson, Phys. Rev. 89, 316 (1953); 90, 717 (1953).
7. G. Racah, Phys. Rev. 61, 188 (1942). Equation (12).
8. J. M. Blatt and W. F. Weisskopf, Theoretical Nuclear Physics. Wiley and Sons, New York, 1952, p. 790.

AN E1 TRANSITION IN U^{239}

Richard Lessler

Bombardment of 1-mil U^{238} foil with 14-Mev deuterons produced U^{239}. The uranium was separated from the other elements by ether extraction and an anion column.

U^{239} ($t_{1/2}$ = 23.5 min) decays with a 1.2-Mev β^- followed by a 74-kev gamma ray. The time between the beta and the gamma was found to be not more than 5×10^{-9} seconds, which was the limit of the coincidence setup. Axel and Dancoff's formula gives $t_{1/2} = 4 \times 10^{-13}$ seconds for an E1 transition and 1×10^{-7} seconds for an E2. Therefore an E1 transition is indicated for the 74-kev gamma ray.

The gamma spectrum of the U^{239} was examined and no other gamma rays were seen. Absorption experiments were done to see if there was a gamma ray under the escape peak (about 45 kev). The results indicated that there is no gamma ray there. However, a gamma ray of less than 10 percent abundance would not have been seen.

The L_I, L_{II}, and L_{III} peaks were seen on the double focusing beta-ray spectrometer. The L_{III} peak was resolved from the $L_I + L_{II}$ peak. Various results all gave a ratio of 5 to 1 for the $L_I + L_{II}$ to L_{III} ratio. Interpolation of Gellman's tables gives the following:

	E1	E2	M1
$\alpha_{L_I} + \alpha_{L_{II}}$	0.195	30.8	16.3
$\alpha_{L_{III}}$	0.076	16	0.020
α_L	0.27	47	16.3
$\alpha_{L_I} + \alpha_{L_{II}}/\alpha_{L_{III}}$	2.6	1.6	815

The ratio $\alpha_{L_I} + \alpha_{L_{II}}/\alpha_{L_{III}}$ again indicates that we have an E1 transition.

Slatis has measured α_L and if we change his value to the present-day definition of α_L it comes out 0.18. Kahn has measured $\alpha_L = 0.20$ and it appears that this value is too low, as he used some poor values in his calculations. At any rate, only an E1 transition comes close to these values for α_L.

Np^{241}

At the present time alpha bombardments of U^{238} foil are being used to produce Np^{241}. The results of the gamma spectra are not too good owing to the presence of a large amount of Np^{239}. There appear to be definite gamma rays at 950, 580, and 450 kev, with about another dozen possible gamma rays. Work to clear up the decay scheme is continuing.

HALF-LIFE AND GAMMA SPECTRUM OF Am^{238}

Robert J. Carr

The half-life and gamma spectrum of Am^{238} are currently under investigation. This nuclide decays by electron capture (alpha branching is less than 1 in 10^5 disintegrations) with a half-life previously reported as 2.1 hours.[1]

The activity was produced by bombardment of Pu^{239} with 27-Mev and 35-Mev protons in the 184-inch synhcrocyclotron. The separation of americium from rare earth fission products was effected by elution from an ion-exchange column packed with 4 percent cross-linked Dowex-50 cation-exchange resin with saturated hydrochloric acid containing 20 percent by volume of ethanol;[2] the remainder of the chemical procedure as well as the bombardment technique was that described by Higgins.[1]

The decay of the gamma spectra was followed on the 50-channel differential pulse-height analyzer, a thallium-activated sodium iodide crystal and a xenon-filled proportional counter tube serving as detectors.

Two prominent gamma rays of 580 and 980 kev were observed on each of the two bombardments. Plotting the logarithm of the integrated intensity of each of the two peaks from each of the two bombardments as a function of time and—for the lowest-energy peak from the lower-energy bombardment—making a small (less than 10 percent) correction for a 12-hour (Am^{239}) component gave a half-life of 1.86 ± 0.09 hours. This value is probably more reliable than that of Higgins (2.1 hours), inasmuch as the latter was determined by resolution of a three-component decay curve in which the longer-lived components constituted about two-thirds of the initial activity.

The assignment of these high-energy gamma rays to Am^{238} rather than to Am^{237} was made in view of the fact that the intensity of these gamma rays relative to that of the 6.01-Mev alpha particle of Am^{237}, as measured in the 50-channel differential alpha pulse-height analyzer, decreased by a factor of more than 20 in increasing the bombarding energy from 27 to 35 Mev, whereas their abundance relative to one another did not change within the statistical accuracy of the determination (about 3 percent). Since no 6.01-Mev alpha particles were observed in the lower-energy bombardment, and since at this low (albeit very poorly discriminated) energy the yield of Am^{237} should be zero, it was assumed in the ensuing calculations that the short-lived components of all gamma- and X-ray peaks were due wholly to Am^{238}.

The gamma spectrum in the region from 150 to 400 kev is obscured by very prominent peaks at 225 and 275 kev belonging to Am^{239}. (These gamma rays have been previously reported only as "~0.3 Mev". It is planned to investigate thoroughly the gamma spectrum and decay scheme of Am^{239} in the near future.)

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1 G. H. Higgins, An Investigation of the Isotopes of Americium and Curium (Thesis), University of California Radiation Laboratory Report No. UCRL-1796, June, 1952.

2 G. Choppin, B. Harvey, and S. G. Thompson, unpublished work.

Photon peaks having 1.9-hour components were also observed at 14, 18, and 102 kev. The first two correspond to L_α and L_β X-rays of plutonium, the last probably includes not only K X-rays of plutonium but also gamma rays from transition between the 146- and 44-kev levels known to be in the daughter nucleus Pu^{238} from study of the negatron decay of Np^{238}.

The relative intensities of these peaks, using counting efficiencies determined by Hoff for the scintillation counter and proportional counter, and making corrections for the escape peak of the 102-kev peak as determined by Asaro and for Compton-scattered electrons from the 1-Mev peak in the 600-kev peak, are:

$$I_{1\ Mev} : I_{600\ kev} : I_{102\ kev} : I_{L\ X\text{-}ray} =$$

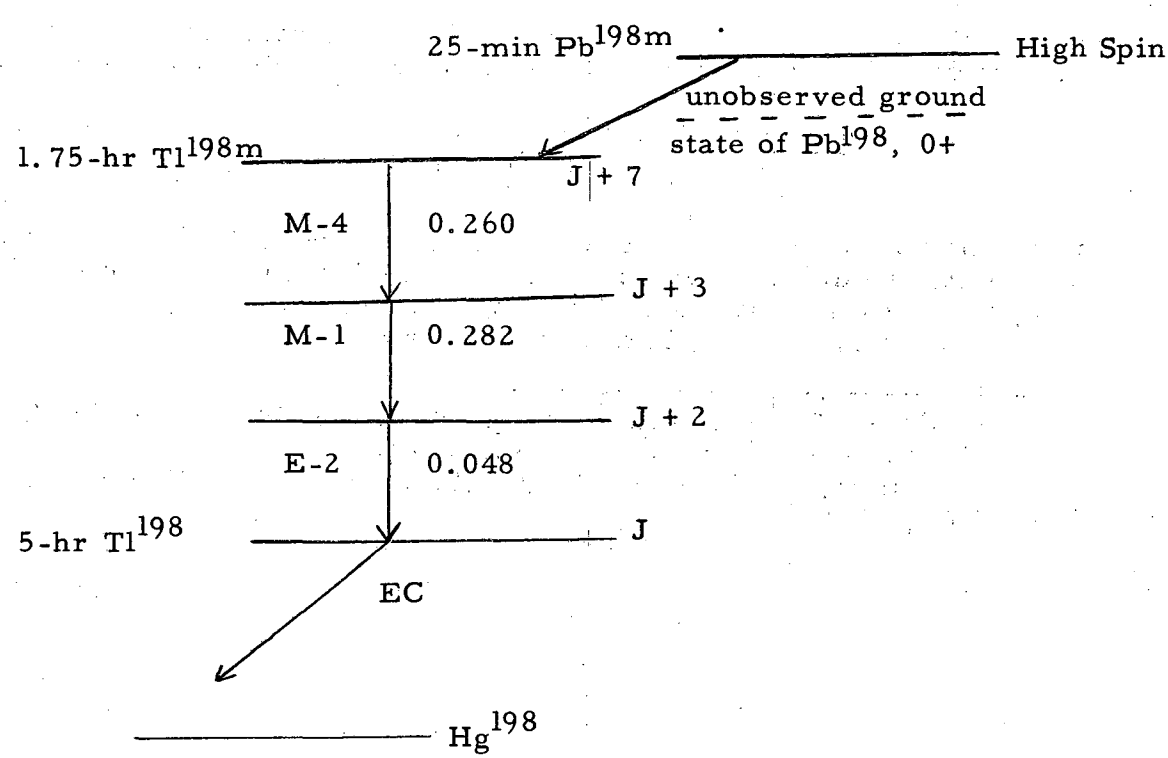
$$0.75 : 0.20 : 1 : 0.59 .$$

In view of the fact that no 600-kev gamma ray is seen in Np^{238} negatron decay, and that 2.2 Mev is available for the Am^{238} decay as compared with 1.42 Mev for the decay of the neptunium, it seems reasonable to hypothesize that the 600-kev level lies above the 1-Mev level. Gamma-gamma coincidence work on this nuclide is in progress, and preliminary results indicate that this is indeed the case.

CONVERSION ELECTRON SPECTRUM OF Tl^{198m}

Thomas O. Passell

The conversion electron spectrum of 1.75-hour Tl^{198m} has been determined on the double-focusing beta-ray spectrometer with a resolution of about 0.5 percent. The data give strong support to the following decay scheme:



DECAY SCHEMES OF Am^{240} AND Cm^{241}

Richard A. Glass, James W. Cobble and Glenn T. Seaborg

Incidental to other studies, the decay schemes of Am^{240} and Cm^{241} are being studied. To date three gamma-ray levels have been seen from the electron capture in Am^{240}: 1.40, 1.02, and 0.9 Mev. The 1.4 and 0.9 levels are also seen from the beta decay of Np^{240}, as well as another level at 0.56 Mev; the 1-Mev level is apparently not populated from this direction.

In a Cm^{240} and Cm^{241} mixture, three gamma rays of 590, 475 and 75 kev have been seen and are probably from levels formed in the electron capture of Cm^{241}.

THE DECAY OF Ir^{192} AND Ag^{110m}

Harold Jaffe and Isadore Perlman

A sample of Ir^{192} has been examined on the 10-inch bent-crystal spectrometer, a 50-channel gamma pulse analyzer, and a gamma-gamma coincidence apparatus. The osmium K X-rays from the electron capture decay were found to be half as intense as the platinum K X-rays. The absolute intensity of the K X-rays was determined as $0.13/\beta^-$. Cork et al.[1] have published the relative intensities of the K conversion electrons from this decay. Setting the sum of the K conversion lines of platinum equal to the intensity of the platinum K X-rays, one can correct the observed osmium X-rays for contribution from internal K conversion. We then calculate:

$$\frac{\text{K capture}}{\beta^-} = 0.02.$$

From the relative intensity of 205-kev gamma rays[2] in the electron capture branch to that of the 316-kev line in the beta decay, one calculates:

$$\frac{\text{Electron capture}}{\beta^-} = 0.09,$$

assuming no electron capture to the ground state of Os^{192}. Therefore, the K/(L + M) capture ratio is about 0.3. Intensity considerations and also analogy to the excited states of the beta-decay daughter indicate that the level of Os^{192} as suggested by Cork should be inverted:

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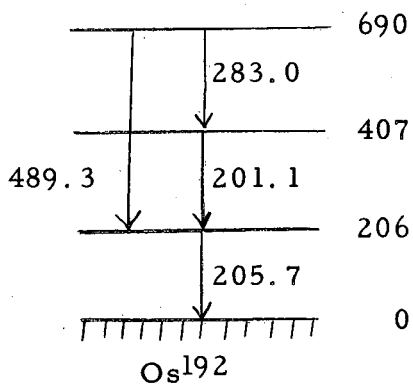
1 J. M. Cork, J. M. LeBlanc, A. E. Stoddard, W. J. Childs, C. E. Branyan, and D. W. Martin, Phys. Rev. 82, 258 (1951).

2 D. E. Muller, H. C. Hoyt, D. J. Klein, and J. W. DuMond, Phys. Rev. 88, 775 (1952).



The conversion coefficients of the five most prominent gamma rays associated with the decay of Ir^{192} have been calculated and are all consistent with an E2 assignment.

Ag^{110m} has also been examined on the bent-crystal spectrometer. The K X-rays of silver and cadmium were observed in the ratio of 2.1:1. Using a calibrated proportional counter connected to a 50-channel differential pulse analyzer, we were able to determine the absolute abundance of K X-rays from Ag^{110m} as 0.037/disintegration. Correcting this figure for fluorescence yield (0.81) and K/(L + M) conversion ratio of the isomeric transition,[3] one calculates the ratio of isomeric transition to beta decay as 0.055.

A search was made for the K X-rays of the electron capture daughter but none was found. These X-rays must be less than 15 percent of the intensity of the silver K X-rays, thus the upper limit for K capture in Ag^{110m} is about 0.5 percent.

COINCIDENCE MEASUREMENTS ON At^{208}

Allen Stoner, Frank Asaro, Frank S. Stephens, and Earl K. Hyde

The complete decay schemes of either the electron capture decay or the alpha decay of At^{208} have not been determined. The alpha-particle energy has been measured by ion-chamber methods and determined to be 5.65 Mev.[a] The gamma spectrum of the electron decay has been shown to contain a 170-kev and 662-kev gamma-ray by Martin, Raby and Hyde.[b] Further information of the decay of At^{208} was obtained in the alpha-gamma and gamma-gamma coincidence measurements described below.

The At^{208} was prepared by extraction from its parent Fr^{212} solution by solvent extraction using tributyl phosphate. The Fr^{212} was isolated from

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3 The K/(L + M) ratio of the isomeric transition was taken as 1.5, an average of the results of K. Siegbahn, Phys. Rev. 77, 233 (1950) and N. M. Anton'eva, A. A. Bashilov, and B. S. Dzhelepov, Doklady Akad. Nauk. SSSR 77, 41 (1951).

a E. K. Hyde, Phys. Rev. 77, 765 (1950).

b Private communication.

a thorium target bombarded with 340-Mev protons. The At^{208} was then mounted on an aluminum foil by volatilization from a platinum plate. The same sample was used for both types of coincidence measurements.

In the alpha-gamma coincidence measurements the sample was placed between a zinc sulfide-coated photomultiplier tube (RCA-5819) and a thallium-activated sodium iodide crystal tube (Dumont-6292). The alpha counter was used to gate the gamma circuit so that only the true coincidence gamma rays were recorded.

In the gamma-gamma coincidence measurements, two thallium-activated sodium iodide crystals mounted on Dumont 6292 photomultiplier tubes were placed opposite each other. One tube was used as the gate and was set to record only the 662-kev gamma ray. The pulses from this tube were used to gate the other gamma circuit so that only the gamma rays in coincidence with the 662-kev gamma ray were recorded. The output from the coincidence circuit was then fed into the 50-channel snapper analyzer[c] in order to determine their coincidence spectrum.

In the alpha-gamma measurements, a 130-kev gamma ray was observed to be in coincidence with the entire alpha spectrum. (See Fig. 1). This gamma ray cannot be seen in the gamma spectrum of At^{208}, owing to the high branching ratio for electron capture decay. This coincidence peak implies the existence of two alpha groups in the alpha spectrum of At^{208}.

In the gamma-gamma measurements, a 170- and a 250-kev gamma ray were observed to be in coincidence with the 662-kev gamma ray. (See Fig. 2.) The 250-kev ray is of low intensity, as would be expected since it was not observed in the gamma spectrum.

ALPHA-GAMMA COINCIDENCE STUDIES OF Fr^{212}

Allen Stoner, Frank Asaro, and Earl K. Hyde

Francium-212 was prepared in order to study the fine alpha structure more closely by alpha-gamma coincidence measurements. The fine structure had been previously determined by Hyde and Asaro,[1] by use of the alpha-ray spectrograph, to consist of 6.339-Mev (24 percent), 6.387-Mev (39 percent) and 6.407-Mev (37 percent) alpha groups. From these data, one could expect coincidence gamma rays of 22 and of 48 or 70 kev.

The Fr^{212} was prepared by bombarding thorium foil with 340-Mev protons. The Fr^{212} was separated from the dissolved target by coprecipitation with silicotungstic acid carrier, and carrier-free Fr^{212} was obtained by use of an ion-exchange column.[2] The Fr^{212} was mounted on a quarter-mil aluminum foil for the alpha-gamma coincidence measurements. The

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c As reported by A. Ghiorso, University of California Radiation Laboratory Report No. UCRL-1959 (September 25, 1952).

1 J. M. Hollander, I. Perlman, and G. T. Seaborg, Revs. Modern Phys. 25, 469 (1953).

2 As reported by E. K. Hyde, University of California Radiation Laboratory Report No. UCRL-1578 (November, 1951).

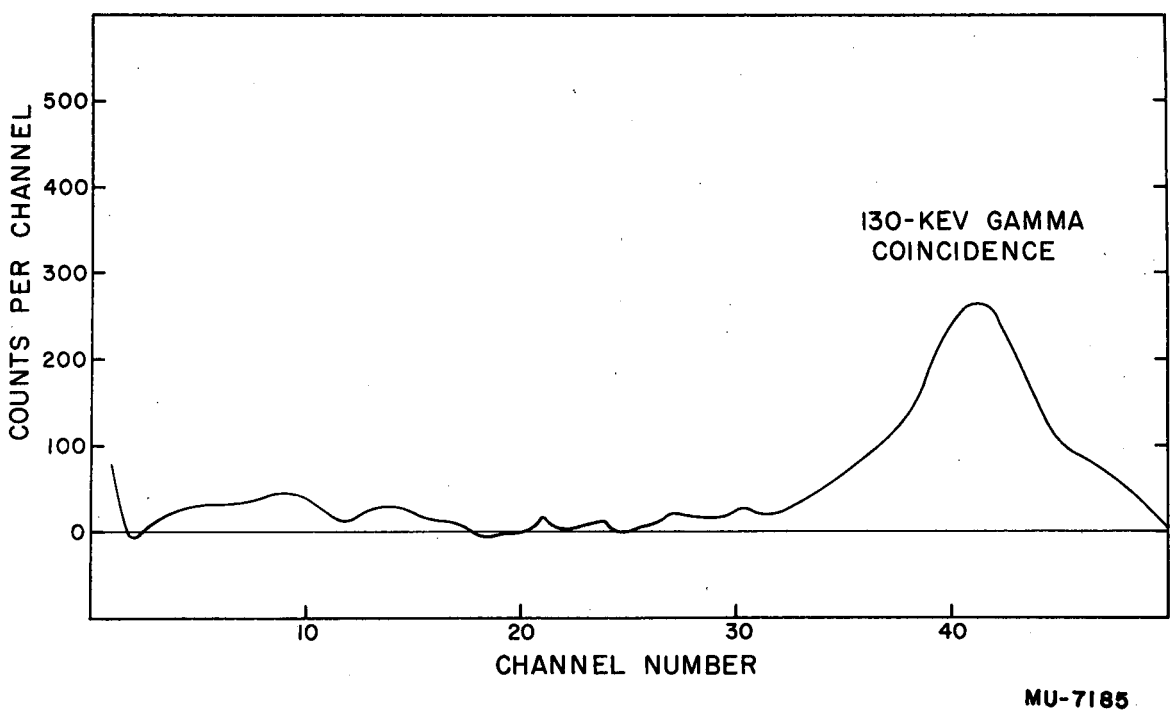

Fig. 1 Alpha-gamma coincidence spectrum of At^{208}. Average alpha counting rate of gate: 2,400/min. Time of run: 100 min.

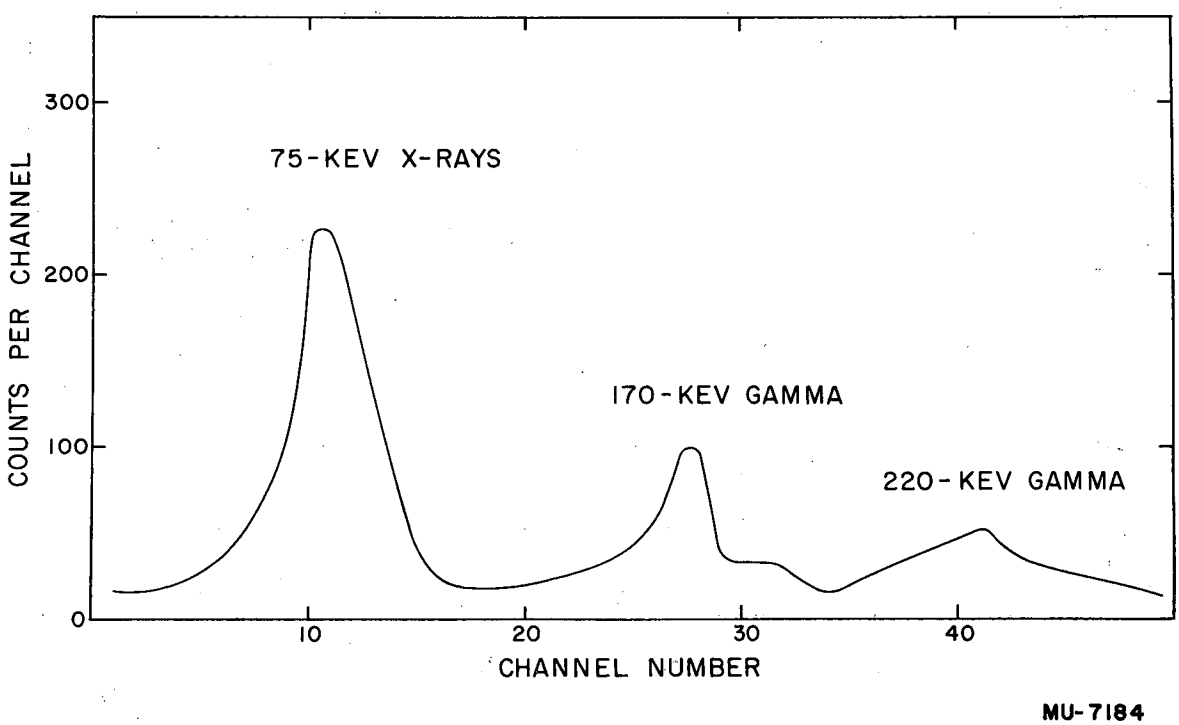

Fig. 2 Gamma-gamma coincidence spectrum of At^{208}, 662-kev gamma applied to gate. Counting rate of gate: 600/min. Time of run: 9 min.

aluminum foil was mounted between a zinc sulfide-coated photomultiplier tube (RCA-5819) and a thallium-activated sodium iodide crystal mounted on a (Dumont 6292) photomultiplier tube. The pulses from the alpha counter were used to gate the gamma counter so that only coincidence gamma rays were measured. The gamma-ray pulses were fed into the 50-channel snapper analyzer[3] to be resolved into energy groups. After corrections for the chance coincidences, the true coincidences were measured.

From the alpha-gamma coincidence measurements, the 70-kev gamma ray and the L X-rays were the most prominent coincidences (see Fig. 1). The 22- and 48-kev gamma rays were not observed, indicating a large conversion coefficient for the former. The intensity of the L X-rays in coincidence also indicates a large conversion. To get absolute ratios, a correction has to be made for absorption of the soft X-rays in the sodium iodide crystal housing and for fluorescent yield. The alpha-gamma coincidence measurements seem to indicate that the present alpha decay scheme is complete.

ALPHA-GAMMA COINCIDENCE STUDIES OF Em^{211}

Allen Stoner, Frank Asaro, Frank S. Stephens, and Earl K. Hyde

Since there was some reason to believe that the alpha spectrum of Em^{211} was not completely determined, a series of experiments was undertaken to establish it more completely. The complex alpha structure had been previously determined by Momyer, Asaro and Hyde,[a] using the alpha-ray spectrograph, to consist of a 5.847-Mev alpha group in 67 percent abundance and a 5.778-Mev alpha ray in 33 percent abundance going to an excited state. The current study of the complex structure was made by alpha-gamma coincidence measurements.

In several bombardments, emanation isotopes were prepared by bombarding thorium metal with 340-Mev protons. After waiting 24 hours for all the short-lived isotopes of emanation to decay, the 16-hour Em^{211} was collected by the glow discharge method[a] on an aluminum foil. From these samples the alpha-gamma coincidence measurements were made, and after chance and counting rate corrections were made, the true coincidences were plotted. The alpha-gamma coincidence equipment consisted of a photomultiplier tube (RCA-5819) which has a thinly coated zinc sulfide window and a thallium-activated sodium iodide crystal tube (Dumont 6292), from which the output is fed into a 50-channel snapper analyzer.[b] The sample was placed between these two tubes and the pulse caused by the alpha particles striking the zinc sulfide was used to gate the gamma counter so that only the coincidence gamma rays were fed into the snapper analyzer.

From the previously reported alpha groups one would expect a 70-kev gamma ray in coincidence with the alpha particles, and this was observed

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3 As reported by A. Ghiorso, University of California Radiation Laboratory Report No. UCRL-1959 (September, 1952).

a As reported by F. F. Momyer, University of California Radiation Laboratory Report No. UCRL-2060 (February, 1953).

b As reported by A. Ghiorso, University of California Radiation Laboratory Report No. UCRL-1959 (September, 1952).

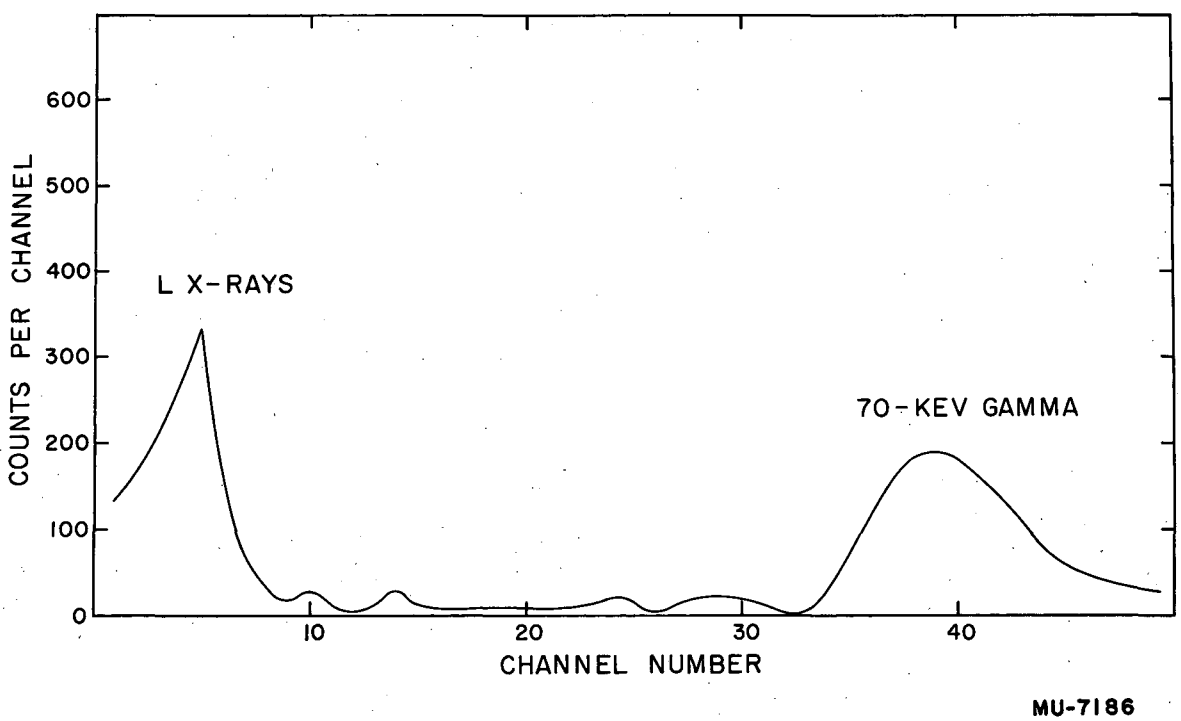

Fig. 1 Francium-212 gamma coincidence spectrum. Counting rate of alpha gate: 8,700/min. Time of run: 6 min.

(See Fig. 1, page 21). However, two additional gamma-rays of 157 and 224 kev were found. The peaks of these gamma-rays were of lower intensity. Their decay was followed in order to establish that they belonged to Em^{211}. The 67 kev energy difference between these two gamma-rays is close to the 70 kev, but whether these gamma-rays are from one additional alpha group and a crossover or from two new alpha groups cannot be determined absolutely from the present data. However, it is conclusive that there is at least one additional alpha group of low intensity and of lower energy than 5.778 Mev.

GAMMA RADIATION OF Ac^{226}, Ac^{225}, AND U^{236}

James Robb Grover

Actinium-226

Actinium isotopes were prepared by bombarding thorium foil with about 300-Mev protons, followed by the chemical isolation of the actinium by the method used by Hyde.[1] The final column separation was done using Dowex-50, 4 percent cross-linked resin, with 0.43-M ammonium lactate buffer at a pH of 4.00. The resulting activity contained both Ac^{226}($t_{1/2} \approx$ 29 hours) and Ac^{225}($t_{1/2}$ = 10.0 days).

The decay of the actinium was followed on a sodium iodide (Tl-activated) scintillation counter with a 50-channel pulse analyzer. The Th^{226} was milked out and its gamma spectrum observed. From these data, prominent gamma-rays were found in the decay of Ac^{226} at about 155 kev and at about 225 kev. The intensity of the 155-kev gamma-ray relative to the total number of beta disintegrations is about 0.4 to 0.5. The 225-kev gamma-ray is somewhat more prominent still, but mixed with a gamma-ray of similar energy in the decay of Ac^{225}.

Further work on Ac^{226} is in progress; precision beta-ray spectroscopy, and beta-gamma and gamma-gamma coincidences might allow the decay scheme to be deduced. It is also planned to look for alpha branching in the decay of Ac^{226} by attempting to milk the Fr^{222} which would result ($t_{1/2} \approx$ 14 min).

Actinium-225

Allowing the above Ac^{226} and Ac^{225} sample to decay for about two weeks yields the nearly pure activity of Ac^{225} and its daughters. This activity was examined with the 50-channel sodium iodide (Tl-activated) scintillation spectrometer, and a recoil experiment was done wherein the gamma spectrum of the daughter chain of Ac^{225} was observed separately. From these data a prominent gamma-ray of about 225 kev was found in the decay of Ac^{225}. The relative intensity of this gamma-ray is probably somewhat less than 0.22 of the alpha disintegration of the Ac^{225}. Some further work in the way of beta spectroscopy (conversion electrons) and gamma-gamma coincidence counting will be attempted on this nuclide.

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

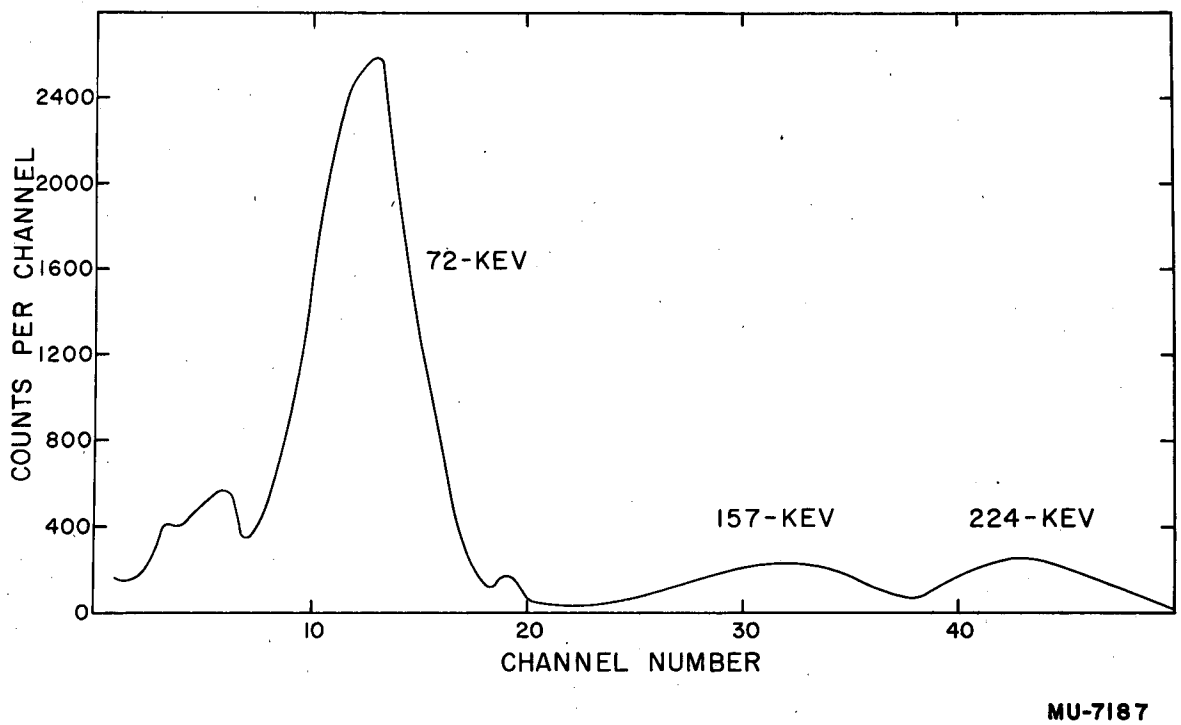

Fig. 1 Alpha-gamma coincidence spectrum of Em^{211}. Counting rate of alpha gate: 58,000/min. Time of run: 65 min.

Uranium 236

About 93 milligrams of impure U^{236} (as U_3O_8, 113.5 mg) was examined with the 50-channel sodium iodide (Tl) scintillation spectrometer; the resulting spectrum was in substantial agreement with that of Bell, et al.,[2] who examined a sample of almost identical composition, also with a sodium iodide scintillator.

Table I gives the mass composition and radiological composition of the sample examined, while Table II compares the results of this work with that of Bell's.

Table I

Mass and Radiological Compositions of the U^{236} Sample

Isotope	Mass Composition, %	Disintegration rate in d/min.	Percent of total disintegration rate
U^{234}	0.15	1.9×10^6	13.4
U^{235}	4.18	1.8×10^4	0.127
Th^{231}		1.8×10^4	0.127
U^{236}	95.31	1.25×10^7	86.3
U^{238}	0.36	2.5×10^2	--

Table II

Observed Results; Comparison with Bell's Work[2]

Observed radiation of U^{236} (kev)	Abundance in total quanta/min.	Estimated total conversion coefficients	Radiation observed by Bell
~12		---	~17
49	8900	~440	51
96	1200	---	93
114	1900	~30	119
(184 belongs to U^{235}, used to normalize)	9800	---	---

2 P. R. Bell, R. C. Davis, J. E. Francis, and M. Cassidy, Physics Division Quarterly Progress Report, Oak Ridge National Laboratory Report No. ORNL-1164, p. 3 (1951).

The abundance values (for U^{236}) are corrected for self-absorption and for the escape peak size according to the experimental work of F. Asaro.[11]

The raw gamma spectrum is dominated by the radiation of U^{235}, in spite of its low radiological composition, on account of the high abundance of its gamma radiation. Therefore, the spectrum of a sample of pure U^{235} was taken, and then normalized to the U^{236} (impure) spectrum by means of the 184-kev gamma ray, which was prominent and alone in the spectrum. After subtracting the two spectra, the resulting spectrum is a composite of U^{234} and U^{236}, and is nearly identical to the U^{234} spectrum. Bell,[2] however, showed that the spectrum is about five times too intense for it to be due to U^{234} alone.

The total conversion coefficient of the 49-kev radiation was computed using the 27-percent alpha branching to the first excited state determined by Dunlavey.[3] This branching is about the same for U^{234}. Gellman's tables[4] of L-conversion coefficients yield the following possibilities:

$$\alpha^{49}_{L\ \mathrm{total}} \begin{cases} E1 = 0.7 \\ M1 = 36 \\ E2 = 380 \end{cases}$$

From the experimental value of 440, the 49-kev radiation appears to be E2. It should be recalled that the radiation is a mixture of that from U^{234} and U^{236}.

The following decay scheme suggests itself, by analogy to the other even-even alpha emitters in this region. (See next page.)

The ratio 163/49 = 3.3 is in agreement with the predictions of the collective model proposed by A. Bohr and B. R. Mottelson[5] as well as with the pattern seen in the other even-even alpha emitters.[6] By using the empirical half-life-vs.-decay energy relationship[10] and Asaro's experimental hindrance relationship,[7] an alpha branching of about 0.4 percent to a possible 163-kev excited state is estimated. From this and the observed abundances a total conversion coefficient of 30 may be calculated. Gellman's values[4] for the L-shell, together with Spinrad's extrapolation points[8] for Rose's tables[9] of K-conversion coefficients, yield the following possibilities.

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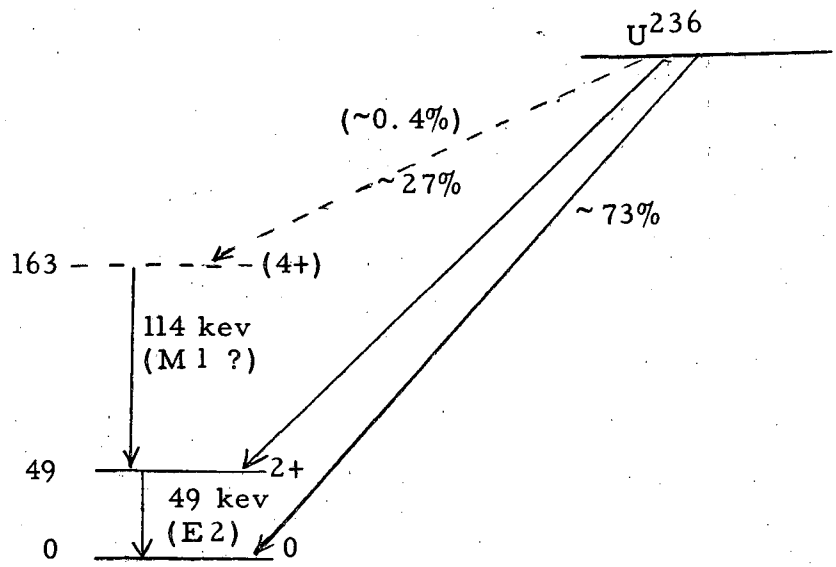
3 D. C. Dunlavey, Ph.D. Thesis, University of California Radiation Laboratory Report No. UCRL-1911, p. 24 (August, 1952).
4 H. Gellman, B. A. Griffith, and J. P. Stanley, Phys. Rev. 85, 944 (1952).
5 A. Bohr and B. R. Mottelson, Phys. Rev. 89, 316 (1953).
6 F. Asaro, Ph.D. Thesis, University of California Radiation Laboratory Report No. UCRL-2180, p. 155 (June, 1953).
7 Ibid., p. 156.
8 B. I. Spinrad and L. B. Keller, Phys. Rev. 84, 1056 (1951).
9 M. E. Rose, G. H. Hoertzel and C. L. Perry, Oak Ridge National Laboratory Report ORNL-1023 (June, 1951).
10 I. Perlman, A. Ghiorso, and G. T. Seaborg, Phys. Rev. 77, 38 (1950).
11 F. Asaro, private communication (1953).



$$\alpha^{114}_{L\ \text{total}} \begin{cases} E1 = 0.07 \\ M1 = 4.5 \\ E2 = 6.2, \end{cases}$$

or, in case the gamma energy exceeds the K-edge of uranium (~116 kev),

$$\alpha^{116\ +}_{L\ +\ K\ \text{total}} \begin{cases} E1 = 1 \\ M1 = 29 \\ E2 = 10. \end{cases}$$

Considering the approximations involved, E2 and M1 are both possibilities, although M2 and E3 should also be considered. Neither is inconsistent with the proposed decay scheme.

A search for higher-energy gamma rays belonging to the U^{236} decay has so far been fruitless.

Further work will be attempted on U^{236}; (1) gamma-gamma coincidence counting to establish whether the two gamma rays are in cascade, and (2) a more concerted search for higher-energy gamma radiation, with special attention to finding an energy state analogous to the apparent (1-) state found in the spectra of some even-even isotopes[11] of thorium and radium.

HEAVY-ION BOMBARDMENTS

Jack M. Hollander

Studies are being continued of the transmutation products resulting from cyclotron irradiations with heavy ions.

Preliminary results from several bombardments of indium (Z = 49) metal with nitrogen ions may be reported. Two new isotopes of barium

(Z = 56) are found in the barium chemical fractions, isolated roughly thirty minutes after the end of bombardment. The resolved half-lives are 12.5 ± 2 minutes and 95 ± 2 minutes.

By making rapid precipitations of cesium silicotungstate away from a 6-N HCl solution[1] of the 95-minute barium activity, we have isolated an active cesium daughter whose half-life is 1.4 ± 0.2 minutes. Hyde and Mathur[2] have recently studied Cs^{123} and Cs^{125}, and have measured their half-lives as 6 minutes and 45 minutes, respectively. It would seem reasonable, then, that the 1.4-minute cesium is the odd-odd isotope, Cs^{126}, and that the parent, 95-minute Ba^{126}, has been produced by the primary reaction $_{49}In^{115}$ (N, 3n) $_{56}Ba^{126}$.

The 12.5-minute barium does not seem to be the same nuclide as the 12-minute Ba^{127} found by Lindner and Osborne[3] from high-energy proton bombardments of cesium, because the genetic relationship which they observed between the 12-minute barium and the well-known 5.5-hour Cs^{127} is absent here, as seen from the fact that there is no 5.5-hour tail in the decay curve of the barium fraction. The new 12-minute barium may be Ba^{124}, produced by the In^{115} (N, 5n) Ba^{124} reaction, but there is no real evidence to support this mass assignment at present. If these mass assignments are correct, however, one can approximate from the counting rates observed the following relative reaction yields:

(N, 2n) <4
(N, 3n) = 50
(N, 5n) = 40

THALLIUM-204

Maynard C. Michel

In view of several conflicting determinations of the half-life of Tl^{204} (2.7 years,[a] 3.5 years,[b] 4.0 years[c]) produced by neutron irradiation of natural thallium, it was suggested that the apparent discrepancies could be due to another isomer of mass 204 or 206 giving rise to a composite decay curve.

A sample of this activity of about 449 curies/gram specific activity was run on the time-of-flight isotope separator to collect mass numbers 204, 205, and 206. In view of the specific activity, it was necessary to run for about 60 hours to collect usable amounts of activity. This required

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1 This procedure was kindly suggested by Dr. E. K. Hyde.
2 E. K. Hyde and H. B. Mathur, private communication.
3 M. Lindner and R. N. Osborne, private communication quoted in Hollander, Perlman, and Seaborg, Revs. Modern Phys. 25, 469 (1953).
a J. M. Hollander, I. Perlman, and G. T. Seaborg, Revs. Modern Phys. 25, 469 (1953).
b K. Fajans and A. F. Voigt, Phys. Rev. 60, 619 (1941).
c G. Harbottle, Phys. Rev. 91, 1234 (1953).

reloading the source and therefore allowed a little more evaporation of neutral particles than is normal with thallium. The effect of this is to reduce the apparent separation factor between adjacent isotopes. However, most of the activity was collected at mass 204, verifying the mass assignment. The activities collected at mass 205 and 206 were less than 2.5 percent and 0.5 percent, respectively, of the activity at mass 204, indicating that the half-life discrepancy, if real, may be due to an isomer of Tl^{204} but cannot be due to isomers of Tl^{205} or Tl^{206}.

Another sample of the same material was run on a conventional mass spectrometer and the isotope abundances determined roughly. The sample was approximately 0.06 percent Tl^{204} by mass, with no isotope of mass 206 present in greater than 0.008 percent of the total. This amount of Tl^{204} is in fair agreement with the specific activity quoted for the sample. It is planned to determine both the specific activity and isotopic abundance more accurately in order to determine the half-life by another method.

Work has continued on the development of more efficient ion sources for use in the time-of-flight separator, some success recently having been achieved with a very high-current bombardment source.

MECHANISM OF LOW-ENERGY (α, xn) AND (α, fission) REACTIONS

Richard A. Glass, James W. Cobble and Glenn T. Seaborg

Considerable progress has been made on the study of the competition of fission with (α, xn) reactions on Pu^{239}. Accurate absolute cross sections for the formation of Cm^{240}, Cm^{241}, Cm^{242}, Am^{240}, and Am^{242m} are being measured. Precise values cannot be given at this time since decay of some nuclides has not yet progressed far enough for proper pulse analysis of the isotopic mixture involved, but preliminary estimations show that the (α, n), (α, 2n), and (α, 3n) cross sections have about the same low value of a few millibarns for 37-Mev alpha particles, in agreement with a previous observation by Street.[1]

Surprisingly, the (α, p2n) reaction had a higher cross section than the (α, 3n) reaction at this same energy. All these results are in agreement with the hypothesis that fission competition, proportional to the Z^2/A factor for each parent compound nucleus, is responsible for determining both the low magnitude and relative values of the particle reaction cross section in the heavy elements. The study at lower energies is in progress.

Fission-product analysis is being carried on at each energy for Ba^{140}, Sr^{89}, and Cd^{115m}, and the total fission cross section for each energy will be determined by doing two complete fission product analyses at two energies, thus calibrating the cross section in terms of the three above key isotopes (two peaks and a valley) for all other energies.

It is expected that this same type of study will shortly be initiated on U^{233}.

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1 K. Street, Jr., Ph.D. thesis, University of California Radiation Laboratory Report No. UCRL-301 (March, 1949).

THE STRUCTURE OF MO_2^+-TYPE IONS

James W. Cobble and Mary J. LaSalle

The entropy of pervanadyl ion, VO_2^+, has been determined as part of a program of collecting thermodynamic data for ionic species which are structurally similar to actinide elements, but which do not contain "f" electrons in their uncompleted electron shells. The entropy was determined calorimetrically from the reaction:

$$V_2O_5 + 2H^+ = 2VO_2^+ + H_2O, \qquad \Delta S = -25 \text{ e.u.}$$

and has the value of -5 ± 1 e.u. This value is so similar to that reported for NpO_2^+ by Cohen and Hindman[1] of 0 e.u. that it serves as a check to these later workers' results as well as to the correctness of writing the formula of the pervanadyl ion as VO_2^+ rather than as a further hydrated species, e.g., $V(OH)_4^+$.

More direct evidence on the correct structure is being obtained from Raman spectra of solutions of pervanadyl perchlorate.

STUDIES OF THE SOLVENT-EXTRACTION BEHAVIOR OF THE TRIVALENT RARE EARTHS INTO TRIBUTYL PHOSPHATE FROM HYDROCHLORIC ACID

Peter Gray

The extraction of the trivalent rare earths, yttrium and scandium, into tri-n-butyl orthophosphate, hereinafter referred to as TBP, has been investigated as a function of hydrochloric acid activity.

The data for the extraction of lanthanum, cerium, promethium, europium, gadolinium, terbium, holmium, erbium, thulium, ytterbium, lutetium, yttrium, and scandium are shown in Fig. 1, in which the log. of the distribution ratio (the concentration in the organic phase divided by the concentration in the aqueous phase at equilibrium) is plotted against the mean specific activity of hydrochloric acid. Below an activity of 1.7 no differentiation in behavior was evident.

The order of increasing extractability is seen to be identical with the order of increasing atomic number with the exceptions of yttrium and scandium. However, these elements appear in their proper position when a consideration is made on the ionic radii of the rare earths. Yttrium has an ionic radius approximating that of holmium and dysprosium, whereas the radius of scandium is smaller than that of lutetium.

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1 D. Cohen and J. C. Hindman, J. Am. Chem. Soc. 74, 4682 (1952).

Qualitative migration experiments in concentrated hydrochloric acid have indicated the presence of negative ions of the heavier rare earths, possibly indicating a complex anion of the rare earth and chloride ions.

Furthermore, the position of yttrium between terbium and holmium in its extraction properties is an indication that the extracting species may be ionic in nature, since according to the reasoning of Marsh,[1] the position of yttrium in the vicinity of holmium implies ionic character of the yttrium and rare earth species as opposed to covalent character which would result in yttrium's appearing as similar to neodymium and samarium.

Because of the similarity of the species involved, it was considered expedient to study the extraction of ferric iron into TBP from concentrated hydrochloric acid. In concentrated hydrochloric acid, ferric iron forms an anion ($FeCl_4^-$),[2] which is thought to be ionic in nature. Consistent with the ionic radius of the ferric ion, ~0.6 Å, (Sc = ~0.8 Å), the ferric complex extracted almost quantitatively into the TBP from concentrated hydrochloric acid. Furthermore, $FeCl_4^-$ is thought to extract into ether as an ion pair, $H^+FeCl_4^-$, and if the extraction into TBP is similar, it may indicate that the order of increasing extractability into the TBP with decreasing ionic radius is due to differences in the association constants of the complex rare earth chloride ion pairs, i.e., the association constant of lanthanum is greater than that of yttrium, which in turn is greater than the constant of lutetium, etc.

Previously a discontinuity was reported in the extraction of the lanthanide rare earths into TBP from 12-N HCl, the discontinuity appearing at holmium. This discontinuity was in error, and it now appears that the relation should be a smooth function. The quantitative determinations of the holmium in the organic and aqueous acid phases were previously determined spectrographically, whereas new data using tracer Ho^{166} and similar radiochemical techniques as used with the other elements resulted in the new value for holmium.

At the present time insufficient data are available on the analogous discontinuity between curium and berkelium in the actinide rare earths, but it does appear that the anomaly still exists, although the magnitude may be slightly other than reported.

The dependence of the extraction of promethium, americium, yttrium and thulium into TBP from 12-N HCl has been determined as a function of TBP concentration, benzene being used as a diluent in the organic phase. The results are shown in Fig. 2, in which the lines are drawn with a slope of 1.

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1 J. K. Marsh, J. Chem. Soc. 118 (1947).
2 S. Friedman, J. Am. Chem. Soc. 74, 5 (1952).

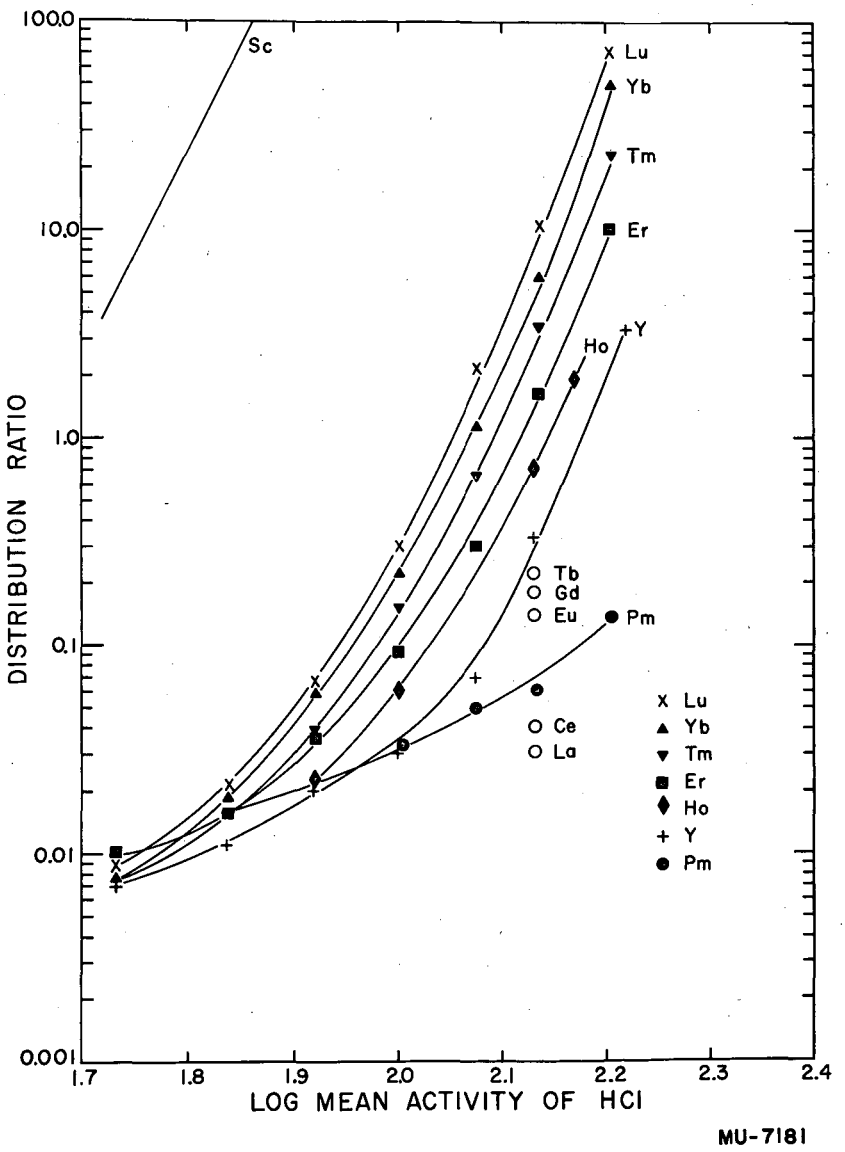

Fig. 1 D.R. into TBP from HCl as a function of HCl concentration.

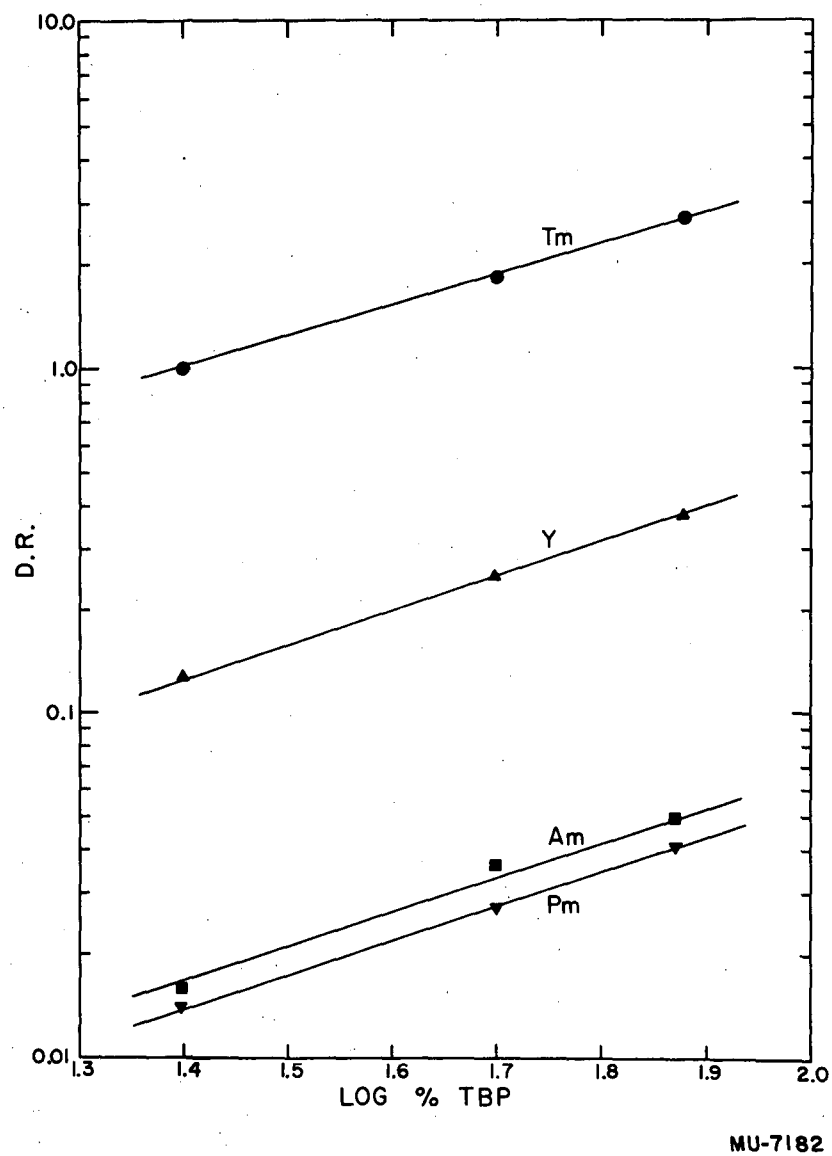

Fig. 2 D.R. into TBP from 12-N HCl as a function of TBP concentration.

CRYSTAL STRUCTURE OF $AuCl_3$

Edward S. Clark

Work is currently in progress on the determination of the crystal structure of auric chloride, $AuCl_3$. The compound was prepared by the reaction of gold and chlorine in the absence of air and water with formation of single crystals by sublimation in vacuum at 200° C. The extremely hygroscopic crystals were transferred to an efficient drybox, and two satisfactory crystals were successfully sealed in Lindemann glass capillaries. Both were plate crystals with cleavage parallel to the (001) pinacoid. A series of Weissenberg photographs were taken (copper radiation, $\lambda = 1.5418$ Å), with rotation about the c-axis covering layers zero through three. Auric chloride was found to be monoclinic, space group $P2_1/c$, C_{2h}^5, with a = 6.57, b = 11.00, c = 6.44 Å, $\beta = 113.3°$, Z = 4. Using multiple film data for the zero layer, I estimated intensities for Bragg planes (hk0) visually and made a Patterson projection on (001). On the basis of symmetry considerations and the Patterson projection, the following rough parameters were proposed for the gold positions: x = 0.042, y = 0.083. Using these parameters, I assigned signs to the structure factors and calculated a Fourier projection on (001). This projection exhibited well-defined electron density peaks for gold and chlorine atoms. From a critical examination of the Fourier projection, the following parameters were assigned:

	x	y
Au	0.042	0.088
Cl_1	0.264	0.996
Cl_2	0.327	0.169
Cl_3	0.792	0.164

Work is continuing at this writing toward the accurate determination of a unique structure for auric chloride.

LATTICE PARAMETERS OF SEVERAL RARE EARTH OXIDES

David H. Templeton and Carol H. Dauben

In the course of our investigations in this laboratory, we have measured the lattice parameters of the oxides of several rare earth elements. The following table gives the values of a we obtained for dysprosium through thulium. The value of a for terbium oxide according to Gruen, Kohler, and Katz[1] and the values previously determined by other workers[2] are included for comparison.

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1 Gruen, Kohler, and Katz, J. Am. Chem. Soc. 73, 1475 (1951).
2 Changed from Kx units. V. M. Goldschmidt, F. Ulrich, T. Barth, and G. Lunde, Structurbericht I, p. 261.

Tb_2O_3	10.718 ± 0.006 Å[1]	10.71 Å[2]
Dy_2O_3	10.667 ± 0.005	10.65
Ho_2O_3	10.607 ± 0.005	10.60
Er_2O_3	10.547 ± 0.003	10.52
Tm_2O_3	10.488 ± 0.003	10.47

The rare earth oxides used were all of greater than 99.9 percent purity and have been spectroscopically analyzed, most of them in this laboratory. They were originally obtained from Iowa State College.

RADIOLYSIS OF ETHERS

Amos S. Newton

The radiolysis products of di-isopropyl ether and dibutyl ether have been run under helium ion bombardments. The products and yields (G in molecules product/100 ev energy input) are given in Table I.

Table I

Radiolysis Products of Some Ethers with 28-Mev Helium Ions

Product	G Di-isopropyl ether	G Dibutyl ether
H_2	2.28	2.71
CO	0.086	0.055
CH_4	0.88	0.061
C_2H_2	0.03	0.024
C_2H_4	0.03	0.128
C_2H_6	0.161	0.036
C_3H_6	1.14	0.125
C_3H_8	0.45	0.123
Butene	>0.007 (iso)	0.379 Butene-1-0.26 Butene-2-0.12
Butane	>0.142 (iso)	0.391 (Normal)
H_2O	<0.05	<0.02
Tot. carbonyl	3.12	0.94
Aldehyde	0.77	----[a]
Ketone	2.35[b]	----

Table I
(cont.)

Product	G Di-isopropyl ether	G Dibutyl ether
Total hydroxyl	0.33	2.06
"Polymer"	0.3[c]	~2.5[c]

a Divergent results on aldehyde in dibutyl ether.
b Ketone by difference. Acetaldehyde and acetone found in gas fraction have been added to amounts found in liquid phase.
c Not volatile at room temperature under a vacuum less than 5 microns. Calculated as molecules of ether from weight of residue. No hydroxyls in residue.

RADICAL REACTIONS IN RADIOLYSIS

Amos S. Newton

One question about which there is some disagreement is the relative importance of radical-radical reactions as compared to reactions of radicals with substrate molecules and direct rearrangements of excited molecules or ions to form the radiolysis products. One check on this is to look at ethane production from molecules where a direct rearrangement is impossible or can be eliminated. Since no formaldehyde was seen from isopropyl alcohol and no acetaldehyde from tertiary butyl alcohol, no molecular rearrangements occur to form ethane in these cases. The alcohols methyl, isopropyl, and tertiary butyl together with acetic acid, methyl iodide, di-isopropyl ether, and isopropyl benzene represent such cases. If one assumes radical reactions, then the following equations can apply:

$$CH_3 + H \rightarrow CH_4 \qquad R_1 = k_1 (CH_3)(H) \qquad (1)$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad R_2 = k_2 (CH_3)^2 \qquad (2)$$

$$H + H \xrightarrow{M} H_2 \qquad R_3 = k_3 (H)^2 \qquad (3)$$

In order to eliminate the concentration of radicals from these expressions since other possible fates of radicals make their values unknown, the expression

$$K_1 = \frac{k_1}{k_2^{1/2} \cdot k_3^{1/2}} = \frac{R_1(CH_4)}{[R_2(C_2H_6) \cdot R_3(H_2)]^{1/2}} .$$

In a competitive system the amount of each product is proportional to its rate of formation, so the yields of methane, ethane and hydrogen can replace the rates of formation of these products. Table II lists the values of K_1 for various systems for which data are available.

Table II

Compound	G			K_1
	CH_4	C_2H_6	H_2	
CH_3OH	0.36	0.014	3.46	1.63
$(CH_3)_2CHOH$	1.14	0.17	2.71	1.68
$(CH_3)_3COH$	1.60	0.52	1.24	1.99
[a]CH_3COOH (anhydrous)	1.38	0.85	0.52	2.07
[b]CH_3COOH (16 N in H_2O)	1.13	0.58	0.58	1.95
[a]$C_6H_5CH(CH_3)_2$	0.078	0.0054	0.311	1.90
[c]CH_3I	0.54	1.03	0.08	~1.9
$[(CH_3)_2CH]_2O$	0.88	0.161	2.28	1.45

a Unpublished experiments, this laboratory.
b Private Communication, Warren Garrison, Crocker Laboratory, University of California Radiation Laboratory.
c R. C. Petry and R. H. Schuler, J. Am. Chem. Soc. 75, 3796 (1953). Data on G values as corrected by Schuler. The ethane value is that calculated from the ratio of CH_4 to C_2H_6 in Table V of this article, Radiolysis with X-Rays.

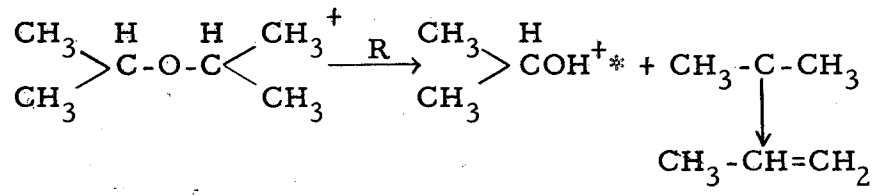
Since the H_2 yields have varied by a factor of 40 and the CH_4 yields by a factor of 20, the constancy of K_1 is strong evidence that radical processes play a predominant part in the radiolysis process. It is known from photochemical results that molecular rearrangements are possible in methane to produce H_2 and HCHO. Therefore, if one assumes that K = 1.95 is correct for a completely radical process one can calculate the hydrogen formed by molecular processes. If one calculates the "molecularly formed hydrogen" by this method one finds 1.0, 0.7 and 1.13 molecules of hydrogen formed by molecular processes for methyl alcohol, isopropyl alcohol, and di-isopropyl ether respectively. The alcohol reactions

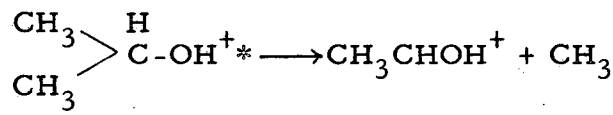
$$CH_3OH \rightarrow H_2 + HCHO \quad (4)$$

$$(CH_3)_2CHOH \rightarrow H_2 + (CH_3)_2CO \quad (5)$$

would account for 60 percent of the formaldehyde and 35 percent of the acetone from these respective alcohols as being formed in this manner, a reasonable correlation if the rearrangement occurs between the hydroxyl hydrogen and carbinol-bonded hydrogen.

The source of the molecular hydrogen from di-isopropyl ether is not so obvious but is understandable from the mass-spectrometer pattern of this compound. The highest peak in the mass spectrum of di-isopropyl ether is 45, and this can only arise from a rearrangement:

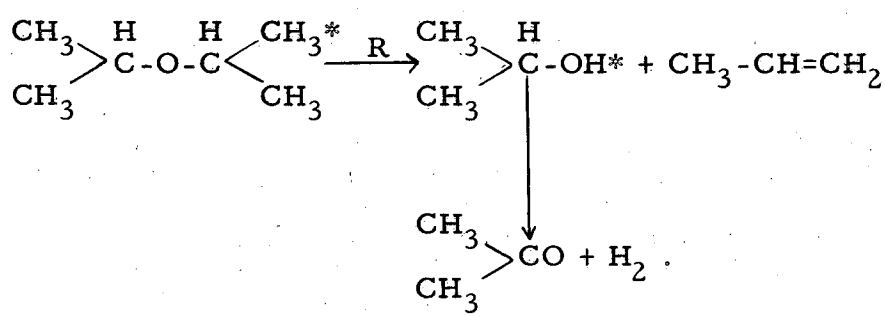




(6)

The ion $(CH_3)_2CHOH^+$ is the molecular ion of isopropyl alcohol and is not very stable even in the lowest state, as shown by the low parent peak in the mass spectrum of isopropyl alcohol, it being only 0.45 percent of the mass 45 peak.

In the radiolysis it is probably not the ion but the excited molecule, both from initial excitation as well as ion recombination, which is effective, and this is not seen in the mass spectrometer. In this case the sequence of reactions would be



(7)

The molecular decomposition of an excited isopropyl alcohol is also postulated for that compound. If this mechanism is true then the yield of "molecular" hydrogen should equal the yield of propylene. These yields are 1.13 and 1.14 respectively. The almost exact agreement is probably fortuitous and both ethylene and molecular hydrogen may be formed by other mechanisms in lesser amounts. The low yield of propane compared to propylene shows reaction (7) to be predominant.

THE CONCENTRATION OF OXYGEN GAS FROM AIR BY SELECTIVE TRANSFER THROUGH STYROFOAM

Amos S. Newton

It has been found that oxygen is transferred through Styrofoam (foamed polystyrene) at a much more rapid rate than nitrogen or argon, hence in principle giving a method of concentrating oxygen without a cryostatic set-up. Only a few simple laboratory experiments have been made to show that it is a real transfer process and that one is not simply removing oxygen that was adsorbed on the surface.

The experimental setup was very simple. A UCRL female water fitting with an inside diameter of about 2 cm was waxed to a glass standard-taper joint for connection to the vacuum apparatus. Over the bottom of the water fitting was placed a piece of Styrofoam about 1 cm thick and a little larger in diameter than the outer diameter of the metal water fitting. Apiezon vacuum compound "Q" was rubbed into the surface of the Styrofoam to seal all pores except for the surface under the hole in the water fitting. The Styrofoam was then sealed to the water fitting with Apiezon Q to form a vacuum-tight seal. This was then evacuated continuously and samples of the gas passing through the Stryofoam membrane were taken periodically for analysis with the mass spectrometer. Since preliminary experiments showed water vapor to be transferred at a much more rapid rate than either oxygen or nitrogen, the air surrounding the diaphragm was dried with Drierite. The results of a 10-day run are shown in Table III.

The mechanism of transfer of the oxygen through the Stryofoam is not known. One experiment in which 48 grams of finely cut Styrofoam was placed in a 3-liter flask and evacuated overnight with a diffusion pump, and then 42 mm air was admitted, showed a ratio of O_2:N_2 in the gas after standing for one hour of 1:4.02, showing the oxygen to be selectively adsorbed. This corresponds to 2.2 ml (STP) of O_2 to be removed. This is about 1.35 percent of the oxygen added. After most of the gas was pumped off the final gas had a ratio of O_2:N_2:A of 1:1.42:0.025, showing that oxygen is the last gas to be removed in degassing the Styrofoam.

Table III

Concentration of Oxygen with a Styrofoam Diaphragm*

Days after initial pumpdown	ml gas/day (STP) (bone-dry basis)	Ratio O_2:N_2:A
0	3.5	1:1.44:-
1	2.0	1:1.37:-
1.25	1.81	1:1.2: :0.028
3.5	1.45	1:0.94:0.023
4.5	0.88	1:0.87:0.023
6	1.0	1:0.96:0.023
7	1.0	1:1.03:0.024
9	1.0	1:1.12:0.024
14	1.0	1:1.02:0.024
Normal air		1:3.72:0.044

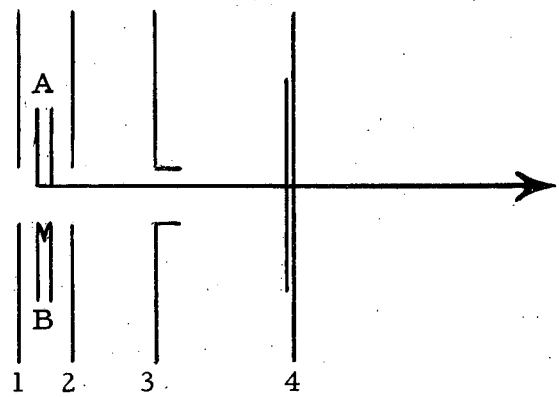
*Effective diaphragm 2 cm diameter, 1 cm thick.

MASS SPECTROSCOPY

Frederick L. Reynolds and Maynard C. Michel

Source Design

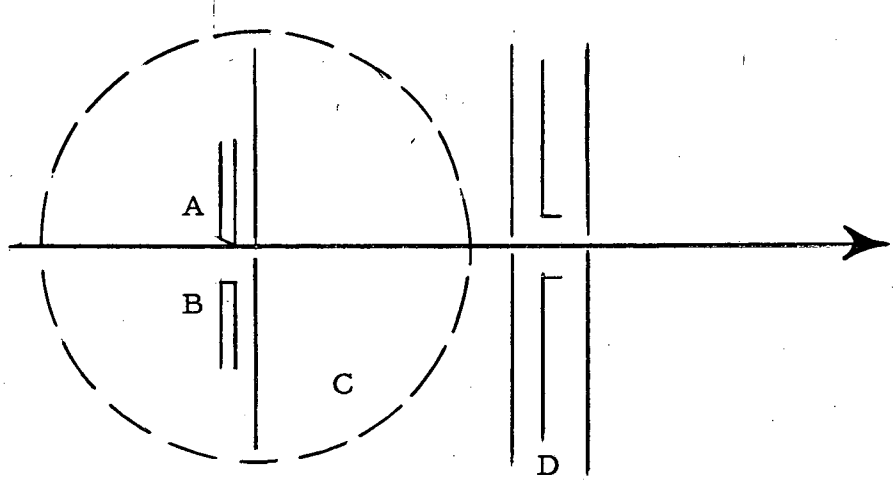
A multiple-filament surface ion source using two filaments instead of the usual three-filament assembly has been constructed for M. S. II. A somewhat similar ion source has been employed by Dr. Barton in M. S. V. The essential features of the design are as follows:



Filament A is a 0.001-in.-thick, 0.030-in.-wide tungsten ribbon operated at high temperature (2500° C). Filament B is a tantalum ribbon, originally 0.030 in. wide, folded into a U shape, and holds the sample charge. Plate 1 and the filaments are operated at 8 kv, plate 2 at 7.4 kv, plates 3 are split plates operated near 6 kv, and plate 4 is at ground potential.

Initial trials with this source using one-half-microgram samples of uranium indicate that the position of filament A relative to the axis of the slit system is critical. The ions seem to appear to be coming from the edge of the hot filament. Dr. Barton reports that because of this phenomenon the beam of ions is very narrow, and from his measurements it is sharper than the 0.010 in. final focus slit.

Barton did not use the folded filament B, but employed instead a similar flat type as used at A. His source arrangement is as follows:



Section C is mounted on a Stevens source probe, section D is permanently mounted to the spectrometer tube. By small-angle rotation of section C the sharpness of the ion beam from filament A could be ascertained. Final work on this source has not been completed, but qualitatively speaking, the over-all efficiency of the source seems to be an improvement over other types tried to date.

In order to more easily study ion-source performance and to study electron-multiplier characteristics, a separate portable vacuum unit was constructed. The operating unit consists of a metal tube 5 in. in diameter, length ≈ 30 in., with easily removable hats at the source and receiver end. At the receiver end a Faraday cup unit, which can be moved in or out of the beam by a stepping relay device, is installed for the purpose of evaluating the gain of multiplier units. By measuring the beam to the cup and from the last stage of the multiplier the gain can be ascertained. The unit allows for outgassing and activation techniques on the multipliers. For these measurements we use a surface ion source coated with a small sample of cesium sulfate, which will give Cs^+ ions at 350° C.

It has been stated by other workers that silver-magnesium multipliers are not easily poisoned by exposure to low-humidity air for periods of one or two hours. Taking a 9-stage multiplier that had never been activated, we found the gain to be only 300. We subjected this unit to an overnight bake-out at 250° C and to a 1-hour bake-out at 350° C. Under these conditions of temperature the unit was subjected to 0.3 mm pressure of oxygen for 15 minutes. The gain of the multiplier after this treatment was 10,000. Letting the unit down to air through a drying-tube inlet for a period of 1/2 hour reduced the gain to 5000. This in a qualitative manner shows the poisoning effect.

OPTICAL SPECTROSCOPY

John G. Conway and Ralph McLaughlin

Zeeman Magnet

The drawings for the arc-spark chamber have been completed and the fabrication job sent to the shops. The chamber will then be attached to a gloved box. The design of the chamber is such as to permit the sparking of radioactive material in the field of the Zeeman magnet.

Low-Temperature Dewar

A double dewar for taking absorption spectra at liquid-hydrogen or liquid-helium temperatures has been finished. Tests using liquid hydrogen have been performed; one filling of hydrogen lasts four days. The dewar has been delivered to the Spectroscopy Laboratory and is being readied for absorption spectra work.

Absorption Spectrum of PuF_3

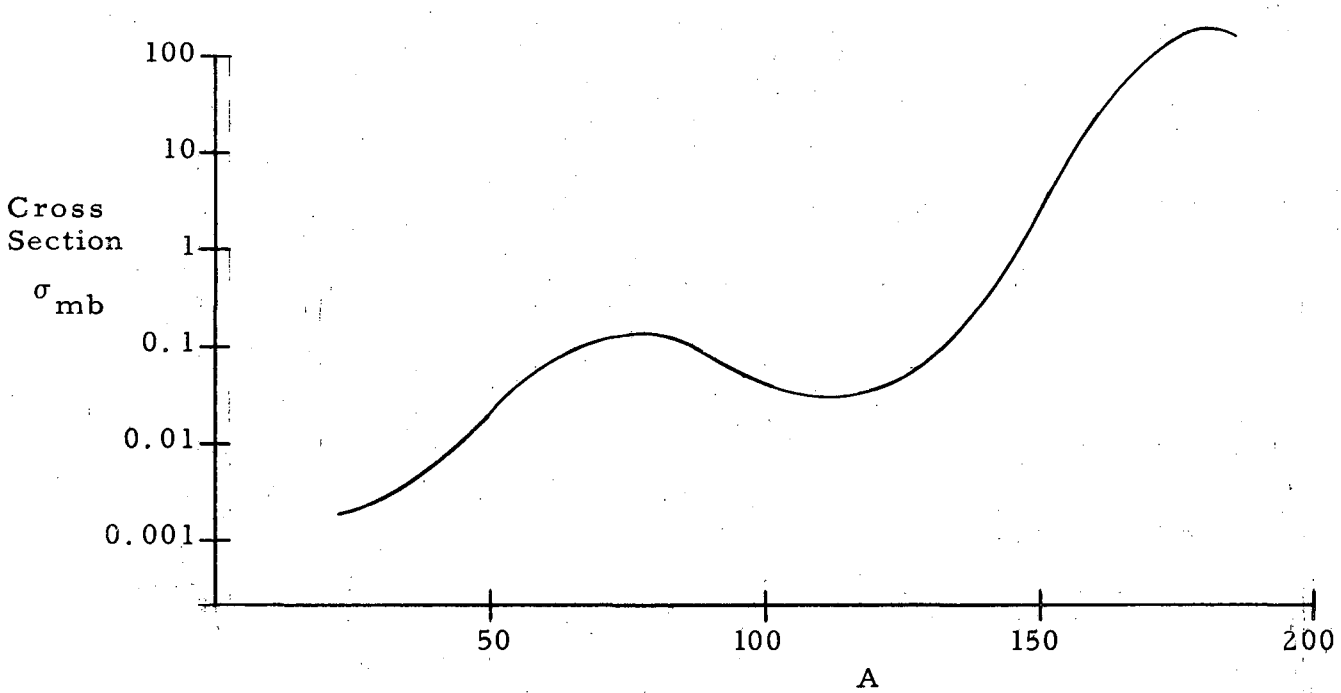
Ninety-five lines were observed and measured in the absorption spectrum of PuF_3 at 77° K in the region 2500 to 9000 Å. The spectrum was so

broad at room temperature that no temperature dependence of lines could be discerned. Six constant differences, some of which could be due to low-lying levels, were located. It is planned to obtain measurements at liquid-hydrogen and liquid-helium temperatures in the hope of placing low-lying levels.

TANTALUM FISSION

Walter Nervik

Investigation of the fission-product distribution of tantalum bombarded with 340-Mev protons is continuing. Elemental fractions of barium, cesium, tellurium, indium, cadmium, silver, rhodium, ruthenium, strontium, rubidium, cobalt, iron, manganese, and magnesium have been separated from the tantalum target material since the last quarterly report. A "thick target" arrangement in which the proton beam traversed a quarter inch of tantalum was used in each of these bombardments, and cross sections for the various nuclides were calculated relative to Ni^{66}. Decay of some of the samples has not progressed far enough for accurate cross sections to be calculated, but those nuclides for which data have been obtained indicate that the cross section-vs.-mass curve has the following shape:



There is a broad maximum in the fission peak near mass 80 with a cross section of approximately 0.15 mb. The saddle between fission and spallation products has a minimum value of approximately 0.015 mb at mass 124. Data on the low-mass-number saddle are incomplete, but there are indications that the minimum is significantly lower than 0.015 mb. Maximum cross sections in the spallation region near tantalum are of the order of 50 to 100 mb, so these fission products represent only a thousandth of the reactions that are occurring in this type of bombardment.

Chain-yield distributions have been rather hard to get because of low cross sections and low counting efficiencies for the neutron-deficient nuclides. The maximum in the chain yield coincides with the maximum isotope-stability line near indium. The observed nuclides of elements with atomic number higher than 49 all lie on the neutron-deficient side of stability, while those of lighter elements are primarily neutron-excess.

A NEW RHODIUM ISOTOPE

Walter Nervik

A previously unseparated activity having a half-life of 2 hr., 16 min. was observed in the rhodium fraction separated from tantalum bombarded with 340-Mev protons. The chemical separation was such that the sample was pure of everything except iridium (which could not have been formed in this bombardment except by secondary beryllium reactions). The activity has also been observed in a full-energy proton bombardment of uranium, but has not been seen in any significant amount in a 7-Mev neutron bombardment of uranium. The activity was not seen at all in an experiment in which uranium was bombarded with 340-Mev protons, ruthenium was separated immediately, the ruthenium fraction was allowed to decay for two hours, and rhodium was milked from the ruthenium.

Analysis of the decay characteristics of this activity indicates that it is a β^- emitter with a beta of approximately 1 Mev energy. Gamma rays of 195, 225, 510, and 1060 kev are probable, and 0.63, 0.715, 1.20, 1.26, and 1.50 Mev possible.

Assuming that this activity has the same counting efficiency as Rh^{105}, its cross section for formation in the tantalum bombardment is approximately 75 percent of that of Rh^{105}, while in the uranium bombardments this ratio is reversed. These facts and considerations of disintegration energies indicate an isomeric state of Rh^{107} as the most probable mass assignment for the nuclide. Because of its peculiar position the activity will be very hard to identify by cross bombardment methods. Attempts to identify it mass-spectrographically have been unsuccessful because of the extremely low ionization efficiency of rhodium. This seems like the most promising method, however, and when new ionization techniques are developed another attempt will be made to separate the activity on the isotope separator.

DOUBLE RETARDING FIELD ELECTROSTATIC BETA-RAY SPECTROMETER

Herbert R. Johnston

General

The originally proposed design of this instrument has been modified with an eye to the reduction of the cost of fabrication. The new design will make use of an existing vacuum system and tank instead of requiring the

construction of a new tank and associated components. This reduces the estimated cost to but a small fraction of the cost of the first design. The new arrangement will, however, still allow the measurement of the energies of beta-particles of 50 kilovolts as an upper limit.

Calculations show that the proposed spectrometer will be very selective. Computed pass band at the half-maximum point is approximately 0.3 to 0.4 percent on an energy basis or 0.15 to 0.2 percent on a momentum basis. If a figure of merit is defined as the ratio of transmission to band pass on a momentum basis, this machine has a figure of merit of approximately 0.75.

In Fig. 1, which is a graphical presentation of the characteristics of all the beta-ray spectrometers listed in reference [1] it may be seen that the proposed spectrometer is much superior in resolution and equal to or superior in transmission to the majority of the flat spectrometers listed. It may also be seen that it is superior in resolution and figure of merit to the majority of helical spectrometers listed.

Gamma Sensitivity of Electron Multipliers

The beta-particle detector to be used in this device is a secondary-emission electron multiplier with eleven dynodes. One of the problems in regard to the use of the multiplier is its possible sensitivity to gamma rays that may be present in a beta-active sample being measured in the spectrometer. A series of experiments were carried out which have furnished a partial answer to this question.

A Co^{60} (γ = 1.33 and 1.17 Mev) sample was used as a source of gamma rays which were arranged to illuminate the first dynode of a Dumont electron-multiplier type photo tube. It was found that the conversion coefficient, or ratio of counts due to gamma rays divided by the total number of gamma rays incident on the first dynode, was of the order of 0.025 percent. A second sample of Am^{241} (γ = 0.06 Mev) was also used to check on the effects of gammas of a different amount of energy. It was found that the conversion coefficient was of the order of 0.035 percent. It may be concluded that the background due to gamma rays in the proposed spectrometer will be small.

During the course of the above experiments, the electron-multiplier tube was cooled by means of dry ice. It was found that the thermal background count was reduced from approximately seventy counts per minute to a fraction of a count per minute. This is a good indication of the effects to be expected in the proposed design, which includes the cooling of the electron-multiplier detector system by radiation from a copper coil placed about the multiplier dynodes and filled with liquid nitrogen.

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1 E. Perseco and C. Geoffreon, "Beta Ray Spectroscopes", Rev. Sci. Instr. 21, No. 12, 945 (1950).

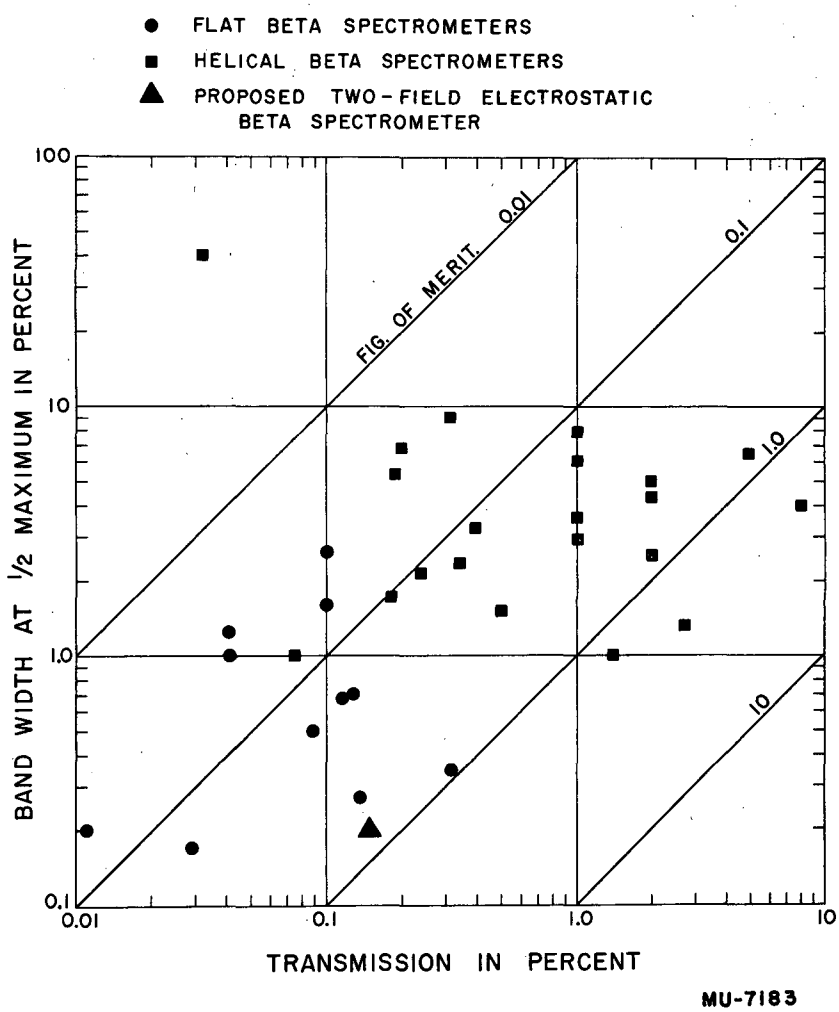

FLAT BETA SPECTROMETERS
HELICAL BETA SPECTROMETERS
PROPOSED TWO-FIELD ELECTROSTATIC BETA SPECTROMETER
FIG. OF MERIT 0.01
0.1
1.0
10
BAND WIDTH AT 1/2 MAXIMUM IN PERCENT
100
10
1.0
0.1
0.01
0.1
1.0
10
TRANSMISSION IN PERCENT
MU-7183

Fig. 1

PRECISION ALPHA COUNTING

Herman P. Robinson and Elinor Potter

A precision low-geometry alpha counter has been constructed and thoroughly tested. The important dimensions are known to about one part in twenty thousand, and the apparatus is sufficiently large (about 38 inches long) that the effects of sample size and position are negligible or easily taken into account. The geometry factor is approximately 2600. Reproducibility appears to be limited only by counting statistics.

Three plutonium samples sent to us from Harwell were counted, and our results differed by +0.05, 0.00, and -0.43 percent from their values. The approximate activities in disintegrations per minute were 8, 2, and 1 x 10^6, respectively.

CHEMICAL ENGINEERING (PROCESS CHEMISTRY)

NOTES ON EXPERIMENTS IN PROGRESS

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

Experiments on the preparation of titanium have been completed. A patent on the film-boiling process has been applied for. A complete report will be given in a thesis entitles "Preparation of Metallic Titanium" to be published soon.

Film Boiling from Subcooled Liquids — Eugene I. Motte, LeRoy A. Bromley

The experimental work for this project has been completed. The theory originally proposed has been found to be in error and a new correlation has been proposed. Writing of this report will start as soon as the data has been calculated for this new correlation.

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

A series of runs has been made with the four-foot pilot-plant scale thermogravitation equipment on ethyl alcohol to determine the effect of change in concentration and temperature level on the separation. Attempts at a theoretical derivation have been so far unsuccessful and an empirical correlation is being attempted.

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

Work has been completed on this project and the report will be issued shortly.

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

Results from the psychrometric study continue to be too erratic to draw a firm conclusion. A new wet-and-dry-bulb assembly has been made from very fine thermocouple wire in an effort to eliminate the stem and radiation corrections which are required with the mercury-in-glass thermometers. No successful runs have as yet been made with the new assembly.

Successful runs have been made on the packed bed drying experiments for the systems air-water, Freon-12-water, and helium-water. These runs would indicate that the Reynolds number is a proper correlating modulus and that the Schmidt number will enter the correlation to the 1/2 power. There may be some uncertainty in surface temperature for these systems. Therefore, it will be necessary to use a low-vapor-pressure material like nitrobenzene to establish this definitely.

A new blower of a higher capacity has been installed in the drying experiment to handle the greater volumetric requirements of helium.

Some data have been taken for the system air-water for mass transfer rates in the one-foot packed column. The packing is 1-1/2 in. Raschig rings.

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

The data collected on the circular tube indicated that f, the fraction of molecules diffusely reflected, varied with the different gases. However, the accuracy of the McLeod gauge in the lower pressure region was not high enough to bring out this variation in the annular sections. A new McLeod gauge was installed on November 8, and data are being retaken for the circular tube and two annular sections.

Solubility Studies — Marshall Cook, Donald N. Hanson

This project has been completed and the results will be published shortly.

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

This project has been completed and the results will be published shortly.

Thermal Conductivity of Gases at High Temperatures — Stephen Whitaker, LeRoy A. Bromley

UCRL-2339 on the thermal conductivities of nitrogen, carbon dioxide, argon, helium, and air from 35° C to 780° C has been completed. The design for the new flange and the copper block (to be used in place of the tin bath) has been completed. The furnace has been altered slightly in order to keep the copper block in a nitrogen atmosphere. At present problems of vacuum casting a silver cell are being worked out.

BIO-ORGANIC CHEMISTRY

M. Calvin, Director

Edited by B. M. Tolbert

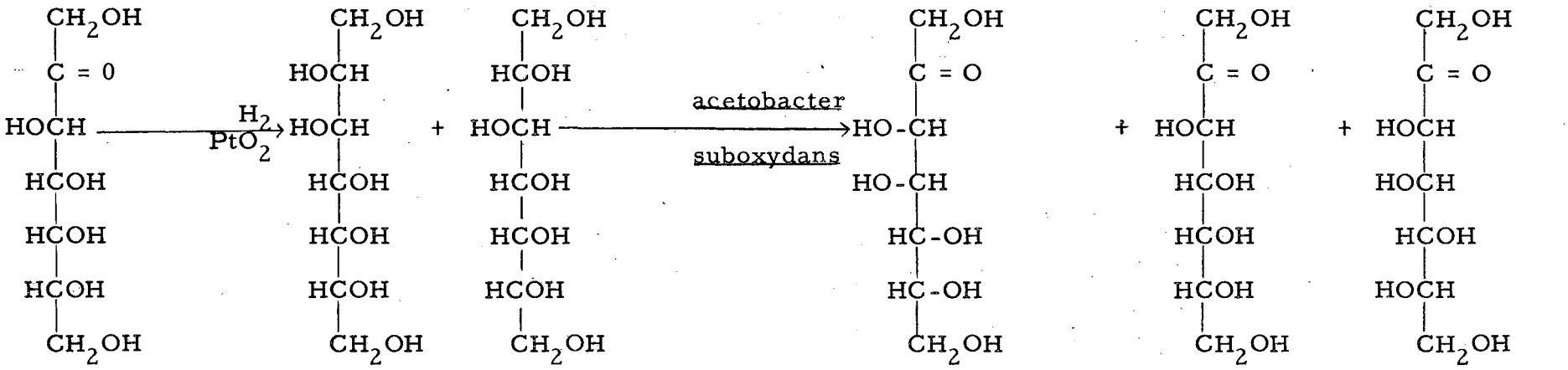
THE DEGRADATION OF SEDOHEPTULOSE

Lorel D. Kay

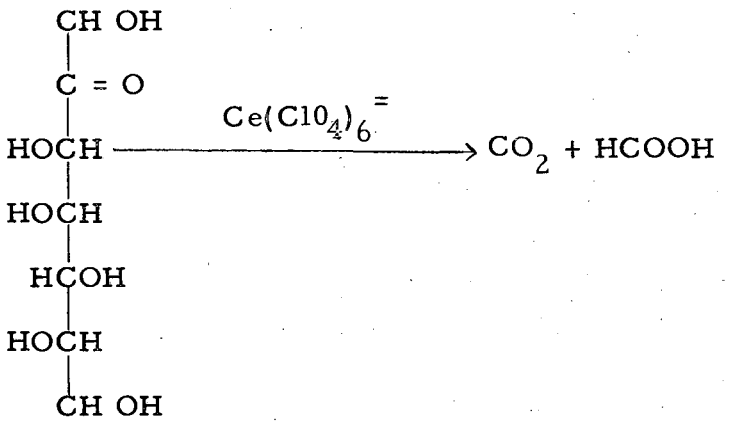
The degradation of sedoheptulose to give carbon number six has been performed. This now gives a series of five reactions (see Quarterly Report for June, July, August, 1953, UCRL-2355) which can be used to obtain all seven carbon atoms of the sugar separately.

Radioactive sedoheptulose was hydrogenated over PtO_2. The hydrogenated product was treated with Acetobacter suboxydans in a small-scale modification of the usual fermentation method. Chromatography of the fermentation mixture gave three radioactive spots which were identified as sedoheptulose, mannoheptulose, and guloheptulose, indicating that the product of the hydrogenation was a mixture of volemitol plus some β-sedoheptitol. Some unoxidized heptitol contaminated the mannoheptulose, and separation of these was not effected. The guloheptulose (which has R_f values very close to fructose in the solvent systems used) was a cleanly separated spot, so it was eluted and oxidized with perchloratocerate ion in perchloric acid to give the keto carbon dioxide. This carbon corresponds to carbon number 6 in the original sedoheptulose.

This series of reactions was performed on a uniformly labeled sample of sedoheptulose and on a sample from a 5-second photosynthetic experiment with soybean leaves. The former sample contained 15 percent of the activity in the carbon dioxide (theoretical = 14.3 percent); the latter sample contained 3 percent in the carbon dioxide. This result confirms our earlier supposition that carbon 6 of sedoheptulose in very short-time photosynthetic experiments contains little label (as is the case for carbons 1, 2 and 7), reflecting the labeling of the α and β positions in phosphoglyceric acid.



sedoheptulose volemitol β-sedoheptitol mannoheptulose sedoheptulose guloheptulose



guloheptulose

SCINTILLATION RADIOAUTOGRAPHY

Andrew A. Benson

The techniques of paper chromatography and radioautography have been combined to give a powerful tool for the study of biochemical reactions, particularly those of phytosynthesis where the readily available $C^{14}O_2$ can be used as substrate. C^{14}-labeled compounds in a filter-paper chromatogram can be counted with a Geiger counter or detected by an X-ray film, but only one third as much β-radiation is emitted from the paper (Whatman No. 1) as from a thin sample on an aluminum plate.

Tritium-labeled compounds are much more difficult to detect on paper because of the relatively greater absorption of its weak β-rays by the cellulose matrix. Only 1/200 of tritium betas are emitted from the surface. A way of avoiding this lack of penetrability has been investigated. The paper and its adsorbed chromatographic spot was saturated with scintillating solvent (terphenyl in phenylcyclohexane, 0.4 percent) and covered with a thin (1/32 in.) glass plate. A sheet of blue-sensitive DuPont singly-coated X-ray film was used to detect the light transmitted through the transparent layer of paper and solvent. A reflecting foil was placed behind the paper to increase reflection of the photons.

Results

The images produced on the film by photography were slightly less well defined than in the radiogram. The use of a cover glass necessarily involves some dispersion. Blue-sensitive X-ray film was found most suitable. Identical exposures to a C^{14} chromatogram gave a radiogram of twice the intensity of the photogram. Identical exposure to tritium-labeled sodium benzoate on paper resulted in images of equal intensity.

These results indicate that development of increased blue-sensitivity will be necessary for successful application of this method. Theoretically it will have its greatest value for tritium chromatography where self-absorption is prohibitively high.

THE CARBOXYLATION REACTION OF PHOTOSYNTHESIS

Andrew A. Benson

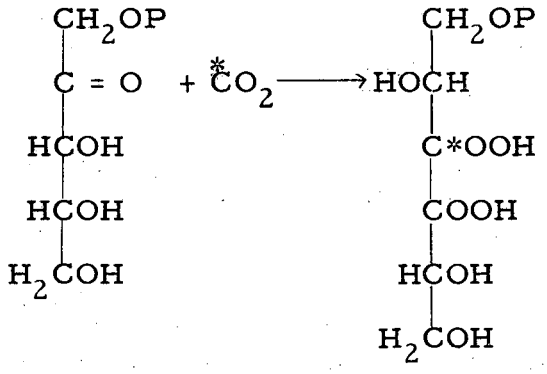
The conclusion that ribulose diphosphate is the primary carboxylation substrate of photosynthesis was developed in the preceding report from this laboratory. The rapid accumulation of this compound when CO_2 was withheld and its rapid decrease upon cessation of the illumination require that ribulose diphosphate is identical or closely associated with the CO_2 acceptor of photosynthesis.

During the transketolase equilibration of heptose, pentose and hexose phosphates which occurs in phytosynthesis, ribulose diphosphate is not formed. ATP is apparently required for phosphorylation of carbon-one. The source

of this ATP may be indicated by the recent findings of Strehler (ORNL) on ATP synthesis during the photochemical reaction,

$$\text{ribulose-5-phosphate} \xrightarrow{ATP} \text{ribulose-1, 5-diphosphate} \xrightarrow{CO_2} \text{2-phosphoglycerate.}$$

This reaction, which leads to the formation of two molecules of phosphoglycerate, is being investigated from a number of directions. Energetically it presents a most feasible entrance point for carbon dioxide.



$\Delta F = -5 \pm 10$ Kcal.

The best available free-energy data for these substances suggest that the carboxylation proceeds readily. Other known carboxylation reactions are much less favorable, having $F^o = +10$ Kcal.

Assimilation Experiments with Ribulose Diphosphate

The possibility of this enzymatic mechanism has been tested. Labeled ribulose diphosphate, isolated paper-chromatographically from Scenedesmus, was incubated at 20° with a brew prepared from an illuminated soybean leaf ground in liquid nitrogen. Labeled sucrose and its precursors were observed in the radiogram of the products.

The Ubiquity of Ribulose Diphosphate in Photosynthetic Organisms

Surveys of the comparative biochemistry of $C^{14}O_2$ fixation carried out in this laboratory have shown that ribulose diphosphate accumulates in many algae, barley leaves, sugar beet leaves and a wide variety of plants. The apparent paucity of ribulose phosphate in soybean leaves, however, cast some doubt upon its function in the process in this plant where sedoheptulose phosphates occur in a remarkably high relative concentration.

Ribulose Diphosphate Accumulation in Soybean Leaves

A small soybean leaf was given $C^{14}O_2$ in saturating light for two minutes. Nitrogen gas was rapidly flushed over the leaf for thirty seconds and the leaf killed in boiling ethanol. Normally, little ribulose diphosphate is accumulated after two minutes' photosynthesis in $C^{14}O_2$. In this experiment a copious accumulation of ribulose diphosphate was observed. Our previous experience with the difficulties of extracting this compound suggested that it may only be obtained by exhaustive aqueous extraction.

Table of Extraction Results

2 min. photosynthesis–30 sec. N_2 soy leaf

Extraction Solvent	Activity Recovered	% Ribulose DIP in Fraction
80% and 20% ethanol extracts	700,000 cpm.	10%
10% ethanol and hot water extract	70,000 cpm.	80%
5% TCA extract	130,000 cpm.	95% of recovered activity

It is seen from the table that an appreciable fraction of the activity is liberated only by TCA extraction. This extract (freed of TCA) did not migrate chromatographically. The material (on paper) was phosphatased to liberate a third of the activity. This was largely ribulose.

It is concluded that ribulose diphosphate is the carbon dioxide acceptor in soy photosynthesis. Its rapid carboxylation and difficult extraction have resulted in past observation of only small amounts of this compound in soy extracts. Phosphorylation of ribulose-5-phosphate by ATP derived from the photosynthetic reaction probably is the source of this compound. Both sedoheptulose-7-phosphate and ribulose-5-phosphate, its precursors, diminish in concentration as ribulose diphosphate accumulates in the absence of carbon dioxide.

UTILIZATION OF ACETATE-2-C^{14} BY THE LIVERS OF NORMAL AND PANTOTHENIC ACID-DEFICIENT RATS

Martha R. Kirk and Melvin Calvin

The distribution of activity in the livers of normal and pantothenic acid-deficient (PAD) rats was discussed in the quarterly report for June, July and August, 1953 (UCRL-2355). Paper chromatography has been used to obtain more definite information about the nature of the radioactive compounds in some of the fractions.

The fatty acid fractions from a number of the livers were chromatographed using one-dimensional chromatography and a propanol–ammonia–water (60:30:10) system (L. Daus, M. Meinke, M. Calvin, J. Biol. Chem. 196, 77,1952). Radioautographs of the resulting chromatograms showed much streaking of the radioactivity, due perhaps to the fact that low levels of activity made overloading the papers necessary. However, rats which had received injections of Coenzyme A, whether normal or PAD, showed fewer short-chain acids than those without such injections.

An aqueous extract made by boiling a portion of the dried liver with water was also chromatographed two-dimensionally, using the classic phenol–plus–water–butanol–propionic acid system. Radioautographs of these chromatograms were remarkably uniform, regardless of the condition of the animal. By spraying the papers with ninhydrin solution and matching the

spots so obtained with the radioautographs we positively identified the following radioactive amino acids: glutamic acid, glycine, glutamine, alanine and valine. Also present, but not radioactive, were aspartic acid, cystine and phenylalanine. One radioactive spot near the origin, which also gave a positive ninhydrin test, was possibly a peptide. Of the three other radioactive spots (which gave no ninhydrin color) two were in the area where one might expect to find lactic and succinic acids, but the other is as yet unidentified. In all cases glutamic acid and glutamine had most radioactivity. There was no detectable difference in the various chromatograms, either in number of spots or intensity, whether the rats had been normal or PAD, with or without Coenzyme A. This is further evidence of the fact that protein metabolism is less affected by pantothenic acid deficiency than is fatty acid metabolism.

THE EFFECT OF HEPARIN ON THE METABOLIC OXIDATION OF ACETATE-2-C^{14} IN RABBITS

Martha R. Kirk and Melvin Calvin

Since rabbits are such important laboratory animals, especially in research on atherosclerosis, it was felt that a more definite knowledge of their general fatty acid metabolism might be interesting and helpful. In particular, we wished to determine the rate at which they oxidize $C^{14}H_3COONa$ to $C^{14}O_2$ and the effect, if any, of injections of heparin on this rate.

To determine the rate of elimination of $C^{14}O_2$ we used a flow system very similar to that described in UCRL-1878 (the Quarterly Report for March, April and May, 1952), for rats. The difference in size between rats and rabbits made necessary a few changes in the system. The smallest possible cage large enough to accommodate a rabbit was used. Airflow rate was increased to 300 cc/min. and the stainless steel ion chamber used in the rabbit experiments had a volume of 257 ml. This chamber had previously been calibrated by filling with air and $C^{14}O_2$ of known total radioactivity and testing on the vibrating-reed electrometer used for the experiments.

Rabbits used were male New Zealand Whites weighing 3.5 kg to 4.0 kg. All injections were made in the ear vein, since results from interperitoneal injections varied widely. The sodium acetate for injection was dissolved in isotonic saline in such concentration that each 0.2 ml of solution contained 10 mg acetate and had an activity of about 20 μc. Heparin used was the sodium salt solution prepared by Lederle Laboratories in a concentration of 100 mg/cc (10,000 units/cc).

Each control rabbit received 0.2 ml acetate solution plus 1.0 ml saline in a single intravenous injection. He was immediately placed in his cage in the flow system and the breath radioactivity was recorded for seven hours. Three rabbits were tested in this manner. Approximately one week later these same rabbits were again tested; at this time each received acetate plus 1.0 ml heparin. Average results of the analysis of these radioactivity curves are summarized below.

Time After Injection	Total % of Injected Activity Eliminated as $C^{14}O_2$	
	Without Heparin	With Heparin
30 min.	7.5%	7.5%
1 hour	12	11
2 hours	35	35
4 hours	50	51
7 hours	56	58

Recovery of $C^{14}O_2$ in the breath of rabbits after injection of $C^{14}H_3COONa$ is somewhat slower than in the rat. Heparin injections have no effect on this rate in normal animals.

The ease with which the electronic system for measuring breath activity was converted for use with larger animals demonstrated to a still greater degree the versatility of usefulness of this method. It has thus far been used successfully for mice, rats, and rabbits.

EFFECT OF X-IRRADIATION OF MICE ON THE CONCENTRATION OF COENZYME A AND DPN-TPN IN THE LIVER

Martha R. Kirk and Edward L. Bennett

Earlier experiments and considerations had indicated that the liver in general, and Coenzyme A in particular, in mice might be unusually susceptible to the effects of whole-body X-irradiation (see previous Quarterly Report, UCRL-2355, for a literature review). Therefore mice were subjected to whole-body X-irradiation and the livers were analyzed for Coenzyme A, DPN-TPN and, in previous experiments, for thioctic acid and glutathione.

The initial experiments had indicated that the concentration of Coenzyme A was particularly depressed after X-irradiation. However, the Coenzyme A values reported for the initial group of mice including the normal, nonirradiated mice were considerably lower than would be expected when compared to Coenzyme A values reported for rat livers.[1] Therefore, the X-irradiation experiments were repeated using male A-strain mice obtained from the animal colony of the Radiation Laboratory.

Table I summarizes the data obtained. It appears from this group of experiments that X-irradiation produced a much smaller effect on the Coenzyme A content of the liver than previously found. Appreciable differences in Coenzyme A content from the controls were found only at the longer time intervals after X-irradiation, i.e., 6 days and 1000 r. As yet, we have no satisfactory explanation for the discrepancy between these and the earlier results. The Coenzyme A content of the normal animals is considerably above that which was previously found, and it is possible that the earlier group had initially markedly depressed content of Conezyme A in the liver

1 Klein and Lipmann, J. Biol. Chem. 203, 101 (1953) report 200 units of Coenzyme A/g of rat liver, although in one series of experiments only 100 units/g was found.

Table I

Coenzyme A Content of Male A-Strain Mice Livers After X-Irradiation

Exp. No.	Irradiation Dosage (r)	Time After Irradiation of Sacrifice (Hours)	No. of Mice	Average Mouse Weight (g)	Average Liver Weight (g)	Average Units CoA/gm. Liver[1]	Average Dev. from Mean
I							
	0		5	19	0.96	169	± 4
	600	72	5	19	1.01	176	± 15
	600[2]	72	5	19	0.98	179	± 15
	600[3]	72	5	19	0.95	181	± 12
II	0	2	5	21	0.98	224	± 16
	1000	2	5	20	0.93	233	± 19
	0	72	3	21	1.08	207	± 24
	1000	72	5	19	0.96	204	± 20
III[4]	0	96	3	18	0.77	289	± 26
	1000	96	5	16	0.81	241	± 16
	0	144	2	19	0.90	237	± 11
	1000	144	5	15	0.92	144	± 14

and were therefore extraordinarily susceptible to X-irradiation. A minor modification was introduced in the analytical procedure in that the liver samples were homogenized and immediately heated in a boiling water bath for 5 minutes and centrifuged, and the supernatant was stored in the deep freeze until analyzed (usually 1 to 3 days later). In the earlier experiments, the homogenized tissue had been immediately frozen in liquid nitrogen and stored in the deep freeze until it was prepared for analysis by thawing and heating an aliquot portion, then it was centrifuged and the supernatant analyzed. However, an experiment in which this procedure was repeated, although yielding slightly lower values for the Coenzyme A content of the liver, did not reveal a large difference between normal and irradiated livers. Also, the rate of destruction of the Coenzyme A in these homogenates on standing at room temperature for several hours was not markedly different.

DPN-TPN analyses were also performed on the livers of irradiated mice 4 to 6 days after irradiation with 1000 r. Only a small decrease in DPN-TPN content of the liver was caused by X-irradiation. The results are summarized in Table II.

2 Three daily injections of pantothine (200 γ) and thioctic acid (100 γ) were made beginning immediately after the end of X-irradiation.

3 Three daily injections of Coenzyme A (200 γ) and thioctic acid (100 γ) were made beginning immediately after the end of X-irradiation.

4 In this experiment, 35 mice were initially X-irradiated. Fifteen mice were sacrificed after 96 hours and 10 mice after 144 hours. Of the remainder, 5 were dead within 6 days after irradiation, and all 10 had died within 8 days.

Table II

DPN-TPN Content of Male A-Strain Mice Livers After X-Irradiation

Irradiation Dosage (r)	Time After X-Irradiation of Sacrifice (Hours)	No. of Mice	Average Mouse Weight (g)	Average Liver Weight (g)	Average γ DPN (g)	Average Dev. from Mean
0	4	4	19	0.86	562	± 12
1000	4	5	14	0.72	449	± 34
0	6	3	20	0.88	497	± 13
1000	6	5	14	0.90	439	± 21

THE SYNTHESIS OF LABELED DIPEPTIDES

Rosemarie Ostwald

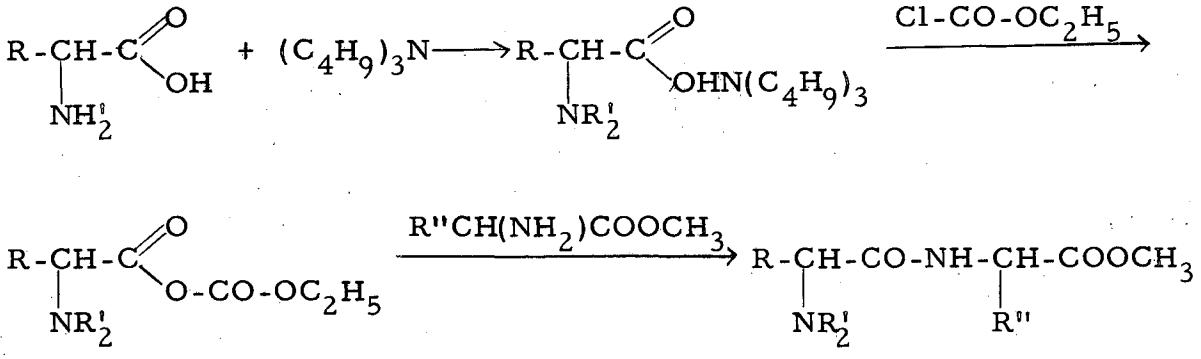
In continuation of the work on the synthesis of carbon-14-labeled peptides (Quarterly Report UCRL-2179) the following experiments were undertaken:

1. Attempts were made to separate alanyl-leucine from leucine and alanine.

The product obtained either by condensation of phthalylalanyl chloride with leucine and consequent hydrolysis with hydrazine, or of bromopropionyl chloride with leucine and subsequent amination, contains both the peptide and its constituent amino acids. This is owing to our inability to obtain the intermediary products, phthalylalanyl-leucine and bromopropionyl-leucine respectively, in pure form.

Two separations of this mixture on ion-exchange columns were tried. Dowex 50 in the acid form was used. In one run the elution was performed with gradually increasing ammonium hydroxide concentrations. All three components, as determined by paper chromatography, came off the column simultaneously, beginning with the first traces of alkali. In the second run, the elution was performed with 1.0-N HCl at a flowrate of 0.11 ml/min. Again all fractions showed all three components. This might be due either to a lack of separation on the column or to a partial decomposition of the peptide by the resin or the acid used. Paper chromatography also separates the mixture of phthalylalanine plus leucine plus peptide or of alanine plus leucine plus peptide. This approach to the problem has been postponed because of the difficulties inherent in its application to large amounts of material.

2. As another approach to the synthesis of peptides, Boissonas' method (Helv. Chem. Acta 34, 874, 1951) utilizing the following scheme was explored:



Phthalylglycylphenylalanine

This compound was prepared as a repetition of Boissonas' work. To 1.36 mmoles phthalylglycine in 4 ml dioxane at 10° was added 1.36 mmoles tri-n-butylamine and, after 5 min., 1.36 mmoles ethylchloroformate. After 15 min. 1.38 mmoles phenylalanine, dissolved in 1.46 mmoles 4.2-N NaOH, was added. After 10 min. at 0° and 30 min. at room temperature the solution was acidified. The precipitate which formed was filtered off and proved to be 0.04 mmole phenylalanine. The filtrate was extracted with ether and the ether evaporated, and the remaining oil was crystallized from isoamyl-alcohol–petroleum ether. The yield of phthalyl-peptide was 50 percent. It had a m.p. of 196°–197° (reported 197°–198°), and it showed only one spot of ultraviolet absorption on a paper chromatogram.

Phthalylalanyl-leucine

When phthalylalanine was condensed with leucine as described above, only a small amount of an unidentifiable oil was obtained.

Phthalylalanylvaline

The preparation of this compound was tried in order to see whether the leucine-containing peptide was peculiarly difficult to obtain. In this case also only a small amount of oil could be obtained under the reaction conditions described above.

3. Since the desired phthalyl-peptides were difficult to obtain by Boissonas' method as well as by the methods described earlier, and also because some difficulties were encountered in splitting off the phthalyl group with hydrazine, the preparation of peptides via the carbobenzoxy (=CBO) derivative was undertaken.

Carbobenzoxyleucylalanine I

To 1.78 mmoles commercial CBO-leucine in 4 ml dry toluene at 0° were added 1.84 mmoles tri-n-butylamine and, after 10 min, 1.88 mmoles ethylchloroformate. The mixture was magnetically stirred at -10° for 30 min., then 1.84 mmoles of alanine dissolved in 1.84 mmoles 4.2-N NaOH was added and stirred again for 30 min. After 2 hr. at 0° and 18 hr. at room temperature, the oily CBO-peptide (together with any unreacted CBO-leucine) was obtained by (1) extraction of the toluene solution with $NaCO_3$, (2)

ether extraction of the alkaline solution, (3) acidification, and (4) ether extraction. Efforts to crystallize the oil from ethylacetate ether were unsuccessful. Paper chromatography showed it to contain one elongated spot only, in the position where CBO-peptide is expected to be, overlapping the CBO-leucine position. The oil was hydrogenated with palladium on charcoal in acidic methanol to split off the CBO- group. The crystalline product proved to be leucine (0.2 mmole) as identified by paper chromatography and analysis (N 10.5 percent, calculated 10.7 percent). No peptide was obtained, because of either the method or the isolation procedure used.

Carbobenzoxyleucylalanine methylester I

This compound was prepared to circumvent the difficulties encountered so far in obtaining pure acylated peptides. The condensation was performed as described above, using CBO-leucine and alanine methylester hydrochloride. The latter was obtained from alanine and anhydrous methanol freshly saturated with gaseous hydrogen chloride at 0°. The solution was allowed to stand overnight, distilled to dryness, and recrystallized from ethanol. The yield of recrystallized produce was 50 percent, m.p. = 141° (theor. m.p., 157°–158°). Chromatographically it proved to contain small amounts of alanine. The alanine ester hydrochloride dissolved in dry toluene with an equimolecular amount of tri-n-butylamine was added to the mixed anhydride. The acylated peptide ester was obtained in 50 percent yield by extraction of the toluene solution with water and sodium bicarbonate, drying, and crystallization by addition of petroleum ether. Its m.p. was 77°–78°, its analysis: C, 62.08 percent; H, 7.64 percent; N, 8.06 percent (Theor.: C, 61.9 percent, H, 7.4 percent; N, 8.04 percent).

Carbobenzoxyleucylalanine methylester II

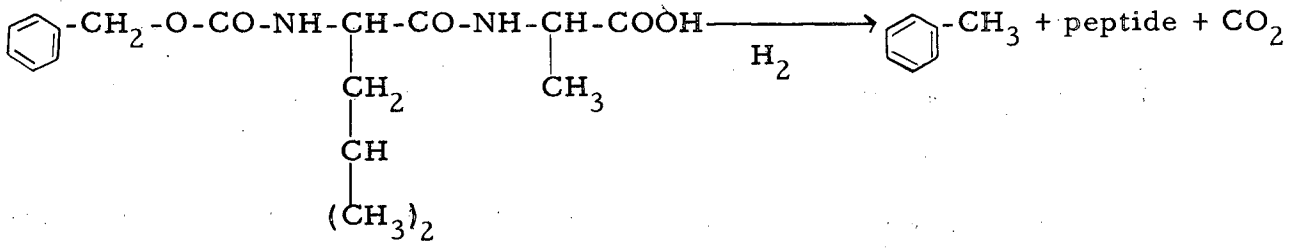
In order to test whether the alanine ester can be used without recrystallization, the same experiment as above was performed with crude alanine-methylester hydrocholride. This was obtained in 90 percent yield by two successive esterifications. The CBO-peptide ester was again obtained in 50 percent yield. Its analysis (C, 62.18 percent; H, 7.21 percent; N, 7.81 percent) remained unchanged when it was purified with 80 percent recovery by repetition of the extraction with sodium carbonate and water. The melting point rose from 74°–78° to 84°–88°. Chromatographically it proved to be free of alanine, alanine methylester and leucine. The presence of unchanged CBO-leucine could not be excluded because the R_f's of the two compounds are very similar in both the butanol–propionic acid–water and the propanol–water solvent systems. Ultraviolet spectra of CBO-leucine and crude and purified CBO-peptide ester, as well as of CBO-peptide, show a maximum at 257 mμ. The extinction coefficients are only slightly different and are not suitable for identification purposes.

Two further experiments showed similar results in yields and properties of product. One of these was performed with radioactive alanine methylester, specific activity 1.05×10^{5} dis/m/mg, containing about 10 percent free alanine from which it was obtained in 94 percent yield.

Carbobenzoxyleucylaline II

The saponification of the CBO-peptide ester was performed in acetone with sodium hydroxide in the cold. After acidification and distillation to dryness, the CBO-peptide was extracted with ethylacetate or acetone to remove the inorganic salt. It was obtained in quantitative yields as an oil or a semi-solid. Chromatographically it proved to be free of alanine, alanine methyl-ester and leucine. The presence of CBO-leucine and CBO-peptide ester cannot be determined by this method because of the similarities of their R_f's in the solvents used.

4. Removal of the CBO-group was accomplished by hydrogenation of the CBO-peptide in acidic methanol at room temperature and atmospheric pressure with palladium on charcoal as catalyst. The progress of the reaction



can be followed by trapping the CO_2 in a calcium hydroxide solution.

(a) In order to test the method, 0.72 mmole CBO-leucine was hydrogenated in 10 ml methanol + 1 ml glacial acetic acid + 1 ml water in the presence of 0.2 g Pd/C, by passing a stream of hydrogen through the solution. After one hour the carbon dioxide evolution stopped. The solution was filtered and the catalyst washed with water and methanol. The product, leucine, was obtained in 70 percent yield by evaporation to dryness.

(b) A recrystallized sample of the CBO-leucylalanine ester (0.54 mmole) was treated as outlined above. Two fractions were obtained. The first one was 0.08 mmole (15 percent) of a product, difficulty soluble in methanol, which behaved chromatographically like leucylalanine (and leucine) and which contained a ninhydrin-positive contaminant with a greater R_f in butanol-propionic acid. Its analysis was: C, 49.9 percent; H, 8.3 percent, N, 12.59 percent. Calculated for leucylalanine: C, 53.8 percent, H, 8.93 percent; N, 13.9 percent; and for leucine: C, 55.1 percent, H, 9.90 percent, N, 10.68 percent. The second fraction consisted of 0.25 mmole (46 percent) of a product, very soluble in methanol, which chromatographically consisted mainly of the compound present as contaminant in (a), and of little of the leucine-similar compound. Its analysis was C, 49.6 percent; H, 8.2 percent; N, 10.98 percent.

(c) A reextracted sample of the CBO leucylalanine ester (0.35 mmole) gave 0.08 mmole (25 percent) of a product which behaved chromatographically like leucine, but which had a lower sensitivity to the ninhydrin spray. The ultraviolet spectrum showed it to be free of any CBO- group. Its analysis was N, 14.19 percent. Unfortunately (see below) the methanol mother liquor was discarded. Because of the poor material balance in the above experiment, another sample (0.40 mmole) of the CBO-peptide ester was saponified

and hydrogenated to give two fractions, which behaved chromatographically like the two fractions described in paragraph b: (a) 0.11 mmole (27 percent), N, 12.89 percent, methanol less soluble; (b) 0.30 mmole (73 percent) detained from the mother liquor of (a) by evaporation to dryness, C, 45.69 percent; H, 7.94 percent; N, 12.02 percent, and 9 percent residue. Both fractions gave on hydrolysis with concentrated hydrochloric acid alanine and leucine; both showed a characteristically different color from leucine when sprayed with ninhydrine containing 10 percent collidine, as do peptides; both gave a positive KI-starch reaction and neither showed a CBO-peak in their ultraviolet spectrum. This test for amino- and amido-nitrogen (H. Rydon, Nature 169, 923,1952), consists of chlorinating the paper with chlorine, blowing off the excess of chlorine, and spraying with a 1 percent solution of KI and starch. Amino acids, peptides, alkylated and acylated amino acids, and peptides and their esters show as strong, blue, transient spots.

5. A sample of the crude radioactive CBO-leucylalanine ester (11.4 μc and 2.18 mmoles) and another sample of the same radioactive CBO-peptide ester after purification, (1.79 mmoles and 9.3 μc) were separately saponified and hydrogenated. Each was fractionally crystallized from methanol. The crude ester gave 6 fractions with a total of 1.5 mmoles (68 percent) and 5.6 μc (50 percent) and a final methanol mother liquor containing 1.2 μc (10.8 percent). The purified ester gave three fractions with a total of 0.71 mmole (40 percent) and 4.62 μc (42 percent) and the final mother liquor containing 2.3 μc (21 percent).

Most fractions consisted of varying proportions of two radioactive compounds, I and II. I was ninhydrine and KI-starch-positive. Its R_f's closely resembled leucylalanine and leucine. II was ninhydrine negative (or very insensitive to this reagent), but KI-starch-positive. Its R_f in phenol was similar to I, in propanol-water, greater than I. Neither compound showed a CBO peak in the ultraviolet spectrum. I, when isolated chromatographically and hydrolized with concentrated hydrochloric acid, showed inactive leucine and radioactive alanine only, in approximately equal amounts, which indicates that it is leucylalanine. II (which was available in mg quantities from the early crystallization fractions) also gave inactive leucine and active alanine on acid hydrolysis. When hydrolized in acetone with sodium hydroxide (repeating the ester saponification procedure), it gave only the original compound back. Titration with alkali indicated that it has no -COOH group. This behavior is compatible with, but not proof for, a diketopiperazine structure of this compound. The analysis (C, 57.02 percent; H, 8.61 percent; N, 14.05 percent) was not conclusive (calculated for diketopiperazine: C, 58.69 percent; H, 8.69 percent; N, 15.2 percent). No such compound was seen in the nonradioactive experiments.

Summary

1. Experiments designed to prepare simple dipeptides by the condensation of phthalyl-amino acids or CBO- amino acids with another amino acid or its ester by various procedures are described.

2. The condensations involving a free amino acid as second partner of the reaction have been abandoned because of difficulties encountered in the separation of the end products.

3. Radioactive and nonradioactive leucylalanine has been prepared in 25 percent yield by the condensation of CBO-leucine and alanine methyl-ester.

4. This preparation contains a major proportion of another radioactive compound. The identification and removal of this compound from the peptide has been undertaken.

5. As the next step in this work it is proposed to prepare leucylalanine and alanyl-leucine, labeled in each of the four possible amino acid residues.

EFFECTS OF IONIZING RADIATION ON CHOLINE AND ITS ANALOGS

Richard M. Lemmon

The abnormal sensitivity of choline-methyl-C^{14} chloride towards its own radiation was reported in our Quarterly Report, UCRL-2179. Further work (Quarterly Report for March, April, May, 1953, UCRL-2257) showed that unlabeled choline chloride also exhibits abnormal radiation sensitivity to 3-Mev electrons and to 1.1-Mev gamma radiation. This work led to interest in ascertaining what effects small changes in the choline molecule might have on its radiation sensitivity. At the present time irradiations have been carried out on acetylcholine chloride, $[(CH_3)_3NCH_2CH_2OCOCH_3]^+ Cl^-$, and on betaine hydrochloride, $[(CH_3)_3NCH_2COOH]^+ Cl^-$. In addition, the physiological importance of choline and acetyl choline has led us to test the radiation sensitivity of these compounds (in the form of the chlorides) in aqueous solution.

Choline chloride

In addition to the β- and γ-irradiations previously reported, aqueous choline chloride has been irradiated with a 3- to 5-Mev electron beam. One gram of choline chloride (Eastman No. 1122) was dissolved in distilled water to give 18.0 cc of solution. The solution was placed in a watch-shaped flask which was connected to a water-cooled condenser (the solution boiled during the irradiation) and was irradiated in the electron beam for five hours. During this time the solution received approximately 1.8×10^8 rep. The amount of decomposition was estimated as 22 percent by isolating (by chromatography) and weighing the 2,4-dinitrophenylhydrazone (about 90 percent of acetaldehyde in water solution can be recovered in this fashion).

Acetylcholine chloride

In addition to the previously reported γ-irradiation of acetylcholine chloride, this compound has been irradiated in aqueous solution. The irradiation of the pure compound (to which a few microcuries of the purified labeled compound was added) was carried out in the same fashion as that previously described (UCRL-2257). The compound received about 5×10^8 rep from the electron beam and a paper chromatogram (using a BuOH-HCl solvent) of a solution of the irradiated material showed the presence of only about 1 percent of trimethylamine. The β-irradiation of the aqueous solution was performed in exactly the same fashion as described above for the

aqueous choline chloride. The acetylcholine chloride solution received approximately 1.7×10^8 rep. An estimation of its decomposition was made by making the irradiated solution alkaline with NaOH, collecting the volatile products in a trap containing a saturated solution of picric acid in ethanol, and filtering off and weighing the resultant picrate (m.p. 210°). The amount of picrate formed indicated a decomposition to the extent of only 1 percent.

Betaine hydrochloride

A sample of betaine hydrochloride was recrystallized (from 90 percent ethanol) until it was analytically pure and had a melting point of 136°–137°. A sample of this material was then irradiated in the electron beam until it had received 6×10^7 rep. The amount of betaine decomposition was then estimated by the analytical procedure of Walker and Erlandsen (Anal. Chem. 23, 1309, 1951). In this procedure the betaine is precipitated as the reineckate, excess reineckate ion is removed by silver ion, and the carboxyl group of the betaine is titrated with standard sodium hydroxide solution. A parallel determination of unirradiated betaine hydrochloride was carried out at the same time that the determination was made on the irradiated sample. The betaine hydrochloride was found to be 14 percent decomposed.

A second sample of the analytically pure betaine hydrochloride was irradiated in an evacuated tube by the γ-radiation of a 110-curie Co^{60} source until it had received 2×10^8 rep. The amount of betaine remaining after the irradiation was determined by the same procedure described above. It was found that 15 percent of the compound was decomposed by the γ-irradiation.

Irradiation data for choline and analogs

The data so far obtained from the irradiation studies carried out on choline and its analogs are summarized in Table I.

Table I

Irradiation Data for Choline and Choline Analogs

Compound	Type of Irradiation	Rep ($\times 10^{-6}$)	Percent Decomp.	Method of Analysis	G (Molecules Decomp. per 100 e.v.)
Choline chloride	C^{14}-β	10.7	63	Paper chrom., picrate, 2,4-DNPH	490
" "	3-5 Mev β	160	51	"	27
" "	1.1 Mev γ	27	67	$CHCl_3$ insol.	207
" "(aq. solu.)	3-5 Mev β	180	22	CH_3CHO-2,4-DNPH	3.5
Acetylcholine chloride	C^{14}-β	10.9	1	Paper chrom.	6
" "	3-5 Mev β	500	1	"	0.13
" "	1.1 Mev γ	24	4	"	10
" " (aq. solu.)	3-5 Mev β	170	1	$(CH_3)_3N$ picrate	0.23
Betaine hydrochloride	3-5 Mev β	60	14	reineckate	18
" "	1.1 Mev γ	200	15	"	5.6

STUDIES ON ADENINE METABOLISM

Edward L. Bennett and Barbara Krueckel

A study of the rates of incorporation and turnover of adenine-4, 6-C^{14} in the soluble nucleotides, desoxynucleic acid (DNA), and ribose nucleic acid (RNA) in C57 male mice has been continued. The duplicate determinations of the specific activities of the adenine of the DNA and RNA of the "Series II" mice (see previous Quarterly Report, UCRL-2355) have been completed and the results are in substantial agreement with those previously reported.

At the present time, we are attempting to develop and refine methods suitable for a more detailed study of the soluble nucleotide fraction. Preliminary experiments have used adsorption of the soluble nucleotides from the cold trichloroacetic acid extracts of various tissues on Darco G-60 charcoal. Subsequently, the nucleotides have been eluted with pyridine–water and concentrated by lyophilization. Two-dimensional chromatography of the concentrated material on Whatman No. 4 filter paper (washed) with butanol–propionic acid–water and subsequently with propanol–ammonia–water has separated 7 or 8 distinct "dark" areas when viewed with ultraviolet light with R_f's equal to or less than 5-AMP in the solvents employed. Tentatively, these include the expected 5-ADP and ATP in addition to DPN, inosinic acid, and guanylic acid. All these compounds contain radioactivity after injection of adenine-C^{14}. A study is in progress of the specific activity of these separate adenine nucleotides as a function of time after the administration of adenine-4, 6-C^{14}, but sufficient data have not yet been obtained to draw any conclusions as to the rate of equilibration of the adenine in these compounds.

In addition to the "dark" areas containing adenine derivatives, there is a "dark" area with a slightly higher R_f than ADP-ATP in the acidic solvent and approximately equal R_f in the basic solvent. Subsequent elution and hydrolysis with dilute HCl has yielded a compound very tentatively identified as uridylic acid. It appears probably that uridine diphosphate or a carbohydrate derivative such as uridine diphosphate glucose is present. Its occurrence in extracts from fresh rat tissue has been reported (R. Caputto, Luis F. Leloir, C. E. Cardini, and A. C. Paladine, J. Biol. Chem. 184, 333, 1950).

STUDIES ON THE SYNTHESIS OF RADIOACTIVE THIOCTIC ACID

Patricia T. Adams

Thioctic acid (6, 8-dithioloctanoic acid) has been synthesized by Brockman, et al. (J. Am. Chem. Soc. 74, 3455, 1952) by the following series of reactions:

$$CH_2{=}CH_2 + ClOC(CH_2)_4CO_2C_2H_5 \xrightarrow[2)\text{heat}]{1)\ AlCl_3} CH_2{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}(CH_2)_4CO_2C_2H_5 \qquad (I)$$

$$\mathrm{I} + CH_3COSH \longrightarrow CH_3COSCH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}\text{-}(CH_2)_4CO_2C_2H_5 \qquad \text{(II)}$$

$$\mathrm{II} + NaBH_4 \longrightarrow CH_3COSCH_2CH_2CHOH(CH_2)_4CO_2C_2H_5 \qquad \text{(III)}$$

$$\xrightarrow{OH^-} HSCH_2CH_2CHOH(CH_2)_4CO_2H \qquad \text{(IV)}$$

$$\xrightarrow[CS(NH_2)_2]{HBr} \underset{\underset{C(NH_2)_2Br}{|}}{CH_2}\underset{\underset{C(NH_2)_2BR}{|}}{CH_2}\underset{\underset{S}{|}}{CH}\text{-}(CH_2)_4CO_2H \qquad \text{(V)}$$

$$\xrightarrow{OH^-} \underset{\underset{SH}{|}}{CH_2}\underset{\underset{SH}{|}}{CH_2}\underset{\underset{SH}{|}}{CH}\text{-}(CH_2)_4CO_2H \longrightarrow \underset{\underset{S}{|}}{CH_2}\underset{\underset{S}{|}}{CH_2}\underset{\underset{S}{|}}{CH}\text{-}(CH_2)_4CO_2H$$

(VI) (VII)

We have attempted without success to adapt this synthesis for the preparation of thioctic acid labeled with either carbon-14 or sulfur-35. On a large-scale preparation, compound IV was isolated and purified for use as an intermediate in the synthesis of the sulfur-labeled compound. It was found, however, that a tenfold excess of thiourea-S^{35} was necessary for the next reaction. A ten- to twentyfold excess of thiourea gave a 10 percent to 20 percent yield of thioctic acid based on the thiol, whereas a twofold excess gave less than 1 percent.

Attempts to adapt this synthetic route to a preparation using ethylene-C^{14} were similarly unsuccessful. The small scale, made necessary by the introduction of radioactivity as such an early stage of the synthesis, made purification of intermediates extremely difficult. None of the compounds could be isolated through vacuum distillation without large losses due to decomposition. Attempts to complete the synthesis without purification of intermediates lead to a product of extremely low yield (2 percent to 5 percent), which is difficult to separate from acidic, polymeric tars formed in early stages of the preparation.

A solid product could be isolated at only one point in the reaction sequence. When the reaction mixture containing compound IV was treated with iodine, a white solid (m.p., 99°–100°) was isolated and shown to be the disulfide of IV (the linear dimer). The yield of this product was about 60 percent from the vinyl ketone (compound I) on a large-scale run when the vinyl ketone had been purified by fractional distillation. But on small-scale preparations where the vinyl ketone could not be well purified, only about 10 percent yield of the crystalline disulfide could be isolated from the viscous, oily reaction mixture. If the pure disulfide is treated with boiling hydriodic acid and excess thiourea, the diisothiuronium salt (compound V) is isolated in 40 percent to 50 percent yield and can be converted to thioctic

acid in about 20 percent to 40 percent yield. This, however, makes the overall yield of thioctic acid from $BaC^{14}O_3$ a fraction of 1 percent, and is therefore not satisfactory as a synthetic method. When crude disulfide was used, only 5 percent yield of compound V was obtained.

Investigation is under way on a synthetic scheme that will allow the radioactive carbon to be introduced at a point much nearer the end of the synthesis. By a series of reactions patterned after the work of Hornberger et al. (J. Am. Chem. Soc. 75, 1273, 1953), it has been possible to prepare a mixture of 3-, 4-, and 5-7 dithiol heptanoic acids. Preliminary experiments indicate that the desired 5-7 isomer can be separated from the mixture by silicic acid chromatography. If this acid can be reduced to the alcohol and converted to the bromide without destroying the 5-membered disulfide ring, a C^{14}-labeled carboxyl group will be added through either the Grignard carboxylation or cyanide replacement reaction.

GENERAL SYNTHETIC ORGANIC CHEMISTRY

Sodium Heptanoate-7-C^{14}

Robert M. Noller

An additional amount of this compound (5.02 mc, 7.23 μc/mg) has been prepared in 37.8 percent yield by condensing methyl-C^{14} iodide with the potassium salt of dihydroresorcinol, splitting the resultant 2-methyl-C^{14}-cyclohexane-1,3-dione with base, and reducing the resultant keto-acid with hydrazine. The synthetic method is described in the Bio-Organic Group Quarterly Progress Report for December, 1952, January, February, 1953 (UCRL-2179).

Morphine and Codeine Glucuronides

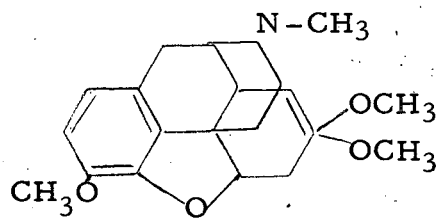
Helen Nelson,
Henry Rapoport

Using codeine and acetobromglucose as models, a method has been worked out for preparing codeine-tetraacetyl-β-D-glucoside, m.p. 190-192°. This method is now being applied to the preparation of the various codeine and morphine glucuronides. The necessary bromo derivative of glucuronic acid has been prepared as follows (Goebel, J. Biol. Chem. 111, 347, 1935; Touster and Reynolds, J. Biol. Chem. 197, 863,1952): Glucuronolactone, with methanol and a catalytic amount of sodium methoxide, gives the methyl ester which is then acetylated and treated with hydrogen bromide in acetic acid to yield methyl-1-bromo-2,3,4-triacetyl-α-glucuronate. This compound is now being condensed with codeine in benzene in the presence of silver carbonate.

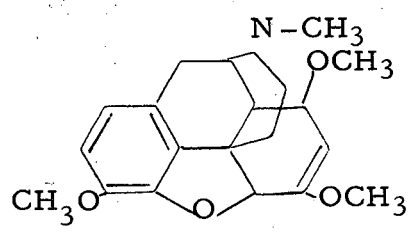
Morphine-7-C^{14}

Calvin Lovell,
Henry Rapoport

The method currently under investigation for the preparation of this compound involves codeinone dimethyl ketal as a key intermediate. A compound of this composition has been prepared and its structure has been proved to be either codeinone dimethyl ketal (A) or 8-methoxy-Δ^6-dihydrothebaine (B). An attempt is being made to distinguish



A



B

between these structures before proceeding to the steps incorporating C^{14}. As a corollary to this preparation, dihydrocodeinone has been treated with trimethylorthoformate and found to yield dihydrocodeinone dimethylketal and Δ^6-dihydrothebaine.

Carbon-14 Ring Labeled Colchicine and Derivatives Don Pack, Henry Rapoport

The objective of this research is to prepare colchicine and colchicine derivatives labeled in ring C with carbon-14. These compounds should prove very useful in studying the unusual biological activity of colchicine in causing chromosome polyploidy and as a mitotic poison.

Preliminary work involved the preparation of N-N-dimethylamino-colchicide, reported in the literature to melt from 203°–205°. Our material melted at 178°–179° and was unchanged by crystallization from six different solvents, sublimation, and chromatography on an alumina column. Chromatography on alumina-impregnated paper revealed only one spot. The optical rotation of our material was identical with that reported for the 203°–205° melting material, and the conclusion was that we had a dimorphic form.

Sodium Butyrate-2-C^{14} Doris Chin

Via propionic-1-C^{14} acid, propyl-1-C^{14} bromide, and carbonation of the corresponding Grignard, 13.8 mc of sodium butyrate-2-C^{14} was prepared in 30 percent yield from $C^{14}O_2$.

Methyl-C^{14} Iodide Doris Chin

Two preparations of methyl-C^{14} iodide were made using lithium aluminum hydride as the reducing agent. The yields were: 26.2 mc, 60 percent yield; and 48 mc, 63 percent yield.

Trimethylpropanolammonium Chloride Doris Chin

The large sensitivity of choline chloride toward radiation degradation has stimulated interest in the stability of other quaternary ammonium salts similar to choline chloride in structure. Synthetic work has started on trimethylpropanolammonium chloride, the next higher analogue, via dimethylpropanolamine.

EFFECT OF β-IRRADIATION ON GLYCINE

Robert M. Noller

As part of our program of studies in irradiation chemistry, a linear electron accelerator (courtesy Synchrotron Physics Research Group) has been used. This unit supplies a maximum beam current of about 2 microamperes and has a mean energy of approximately 3 Mev. Because of the broad and variable energy spectrum of the beam, it has not been possible, as yet, to measure with any degree of accuracy the amount of energy absorbed in a sample. By assuming a monoenergetic beam and measuring the current that comes through the sample, one can determine an approximate order of magnitude. With such necessarily inaccurate assumptions, it has been determined that under optimum conditions the beam delivers between 10^8 and 10^9 rep/hr.

With these limitations in mind, a 1.737-g sample of powdered c.p. glycine was placed in an irradiation cell, evacuated, and irradiated for 2 hours in the beam. The sample probably received about 10^9 rep. During the irradiation, the sample was cooled by an air stream and its temperature did not exceed 60° C. Sufficient space was provided so that excess pressure would not be developed by any gases that might be formed.

The sample was opened in a sealed system and the volatile materials drawn successively through an ice-acetone and a liquid-nitrogen trap by means of a Toepler pump. In order to assist the removal of the volatile materials, the irradiation cell was heated to 100° with a water bath while it was being evacuated. The volume of the non-liquid-nitrogen condensable gases was measured manometrically (5.64 cc STP) and its composition determined with a mass spectrometer (courtesy Dr. Amos Newton).

During the course of this process, some material sublimed out of the irradiation cell and collected on the walls of the glassware. When the irradiation cell was eventually opened (under a nitrogen atmosphere), 28.4 mg of this solid material was recovered. The material on the walls was washed into a volumetric vessel with water. Analysis of the solid for C, H, and N and titration of the remainder indicate that the material was ammonium acetate. The total quantity of material was 0.495 meq.

The material in the ice-acetone trap (41.5 mg) has not yet been analyzed. It apparently consists mostly of ammonium carbonate and some other volatile material.

The material in the liquid-nitrogen trap was drawn successively through a tared Ascarite column, a dry-ice trap, and a liquid-nitrogen trap. The increase in weight of the Ascarite tube plus the weight of material in the dry-ice trap (99 percent H_2O) is assumed to be due only to absorption of CO_2 (79.4 mg, 1.80 mmoles). The gas collected in the liquid-nitrogen trap was analyzed in the mass spectrometer. By dissolving the gas in standard HCl and back-titrating to determine the quantity of NH_3 (1.05 mmoles), it was possible to determine the total quantity of gases.

The material remaining in the irradiation cell amounted to 88.1 percent of the starting weight. A portion of it (380 mg) was dissolved in 5 ml water and made acid with H_2SO_4. After half of this solution had been distilled, the distillate was titrated to determine the quantity of volatile acids (0.133 meq., assumed to be acetic acid). The material remaining in the distillation flask was extracted with ether to remove any non-steam-distillable acidic materials. The residue from the ether extract was taken up in water and alcohol. This was titrated with normal NaOH and found to contain 0.330 meq. H^+. This solution, which had been titrated to pH 11, stood at room temperature for two days. It was then run through a small, carefully washed Dowex 50 ion-exchange column. The eluate was titrated just to the end point and was found to contain 0.692 meq. H^+. This increase in acid equivalence is not understood. When this solution was dried down, the weight of the residue was found to correspond to that which would be expected if it were disodium succinate or some simple derivative thereof. Chromatographic analysis indicates that this material may be malic acid (hydroxysuccinic acid), although another possibility is tricarballylic acid.

The still acid residue from the previous extraction was made basic to phenolphthalein and volatile materials in it were distilled into a standard HCl solution. Back-titration indicated 0.603 meq. H^+ had been used. A possible guess as to the composition of the basic material would be that it was methylamine and ammonia.

A one-dimensional paper chromatogram (butanol–propionic acid–H_2O solvent) of the material from the irradiation cell was run, and then sprayed with ninhydrin. There were at least four other ninhydrin-active spots in addition to that of glycine.

Following is a table listing concentrations of identifiable components in terms of micromoles per 100,000 micromoles of starting glycine. They are grouped according to the initial fractionation scheme.

Non-liquid-nitrogen condensable		Liquid-nitrogen condensable		Ice-acetone condensable	Solid remainder	
CH_2	584	CO_2*	7820	Not analyzed	CH_3-$COONH_4$**	1980
H_2	254	NH_3	4540	CO_2	R-NH_2	10500
CO	47	CO_2	35	NH_3	Malic acid	5410
N_2	22	C_2H_6	22		CH_3-COOH	2320
CO_2	17	Unknown	150			
Air	4					
Unknown	150					

*Calculated from wt. of material absorbed on Ascarite.
**Material which sublimed out.

As yet, most of our analytical tools have not been perfected to the point where anything but semiquantitative information may be obtained. The course of this work has indicated several changes which would enable a more complete and accurate analysis of the products. One major change would be to dissolve the irradiated material in degassed H_2O in order to insure that all occluded gases could be removed for analysis. Another would be to discontinue the use of Ascarite as an absorbent, since it will adsorb many other compounds such as hydrocarbons. Still another, and more obvious, improvement will be the use of C^{14}-labeled starting materials. Yet to be developed, of course, is an actinometer capable of giving us a reasonably accurate idea of how much radiation these samples are receiving.

GENERAL CHEMISTRY

W. M. Latimer, Director

METALS AND HIGH-TEMPERATURE THERMODYNAMICS

Leo Brewer, William Hicks, Richard Porter
Oscar Krikorian, and James Kane

Heats of Formation and Absolute Absorption Coefficients of High-Temperature Molecules

The new King furnace is in operation, and the auxiliary equipment for determination of absolute absorption coefficients and heats of formation of high-temperature molecules is being designed.

Gaseous Carbon Species

The singlet Mulliken system of C_2 has been found in absorption, indicating that the ground state of C_2 may be a singlet. The 4050A cometary bands of C_3 have been studied over a range of temperatures and the heat of sublimation found to be close to that of C_2. A strong continuous absorption in the ultraviolet has been discovered, which appears to be the absorption observed in the ultraviolet spectrum of carbon stars. These studies are being actively pursued to clarify the chemical composition of carbon vapor.

Magnesium Oxide Gas

The main species present in magnesium oxide vapor have been established. The results of this work are being reported in UCRL-2416. Further work is under way using magnesium isotopes to establish a vibrational assignment for the MgO spectrum.

Reflection Coefficients of Molecular Beams

Molecular beams of bismuth, antimony, tin and lead have been reflected from solid surfaces. Although detectable reflection was observed, all sticking coefficients have been practically unity.

Sodium Carbonate Vapor

Knudsen and flow methods of measuring vapor pressures have been used to study the sodium carbonate system. The methods are being refined to yield more accurate results.

Molybdenum Chloride Vapor

Work is continuing on the effect of water on the volatility of molybdenum chlorides.

Refractory Silicides

The work on the ternary diagrams of Si, C, N, and refractory metals has been completed and will be summarized in a report shortly.

BASIC CHEMISTRY, INCLUDING METAL CHELATES

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

Hydrate Complexing of Cr^{+++}

The main research problem involves studying the hydrate complexing of Cr^{+++}. For these studies, an accurate value for the hydrolysis constant of Cr^{+++} is necessary. An attempt was made to measure the hydrolysis constant for the reaction $Cr^{+++} + H_2O = CrOH^{++} + H^+$ by measuring the H^+ concentration. This was done by using a vibrating-reed electrometer in conjunction with a glass electrode. $CrOH^{++}$ polymerizes quite rapidly at the pH where it is necessary to work, H^+ being formed as a result of the polymerization. Therefore the measurements must be made as a function of time and each measurement must be made rapidly. With the above apparatus using a Type E glass electrode, the minimum time to make a measurement was 10 to 15 minutes, which was not rapid enough for our purpose. The slowness seemed to be inherent in the electrodes rather than in the electrometer. The hydrolysis constant will probably have to be measured by a different method.

Another project is the study of the complexing of various metals by fluoride ion. The complexing of Sc^{+++} by F^- was studied at 15° and 35°. The results of these measurements are in the process of being calculated. Studies of the fluoride complexing of Cu^{++}, Zn^{++} and Pb^{++} are under way.

(Because of the graduation of all our students this last year, a new group of Graduate Students is starting new problems in this field, but it will be some time before their research programs are under way.)