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September, October, November 1954

January 10, 1955

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CHEMISTRY DIVISION QUARTERLY REPORT

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Contents

BIO-ORGANIC CHEMISTRY

Quantum Requirement in Photosynthesis Related to Respiration. 4

Constant-Density Culture Apparatus for Unicellular Algae 5

Studies on the Carboxylation Reaction in Photosynthesis. 7

Dark Fixation of CO_2 by Euglena 11

The Utilization of 3-Hydropyruvic Acid by Scenedesmus. 12

Brain Cholinesterase and Adjustive Behavior Patterns 13

An Instrument for Continuous Measurement of Breath-$C^{14}O_2$ Metabolism Rates in Humans. 13

Respiratory Metabolism of Labeled Organic Compounds. 15

The Acute Effect of Nicotine on the Metabolism to $C^{14}O_2$ of Acetate in Normal Rats. 16

A Liquid Scintillation Counter for Tritium Measurement 17

A Pyrrolidine Rearrangement 22

The Synthesis of DL-Thioctic Acid. 25

Leucylalanine-2-C^{14} 25

Effects of Ionizing Radiation on Choline Chloride and its Analogs 27

Radiation Chemistry of Benzoic Acid 29

Irradiation of Thioctic Acid and Bisnor-Thioctic Acid 30

NUCLEAR CHEMISTRY

Studies of the Plutonium-239 Fission Products After Long, Intense Neutron Irradiation 31

Neutron-Deficient Isotopes in the Hafnium-Lutetium Region . . . 35

Radiations of Barium-128–Cesium-128 35

Fast-Coincidence Work on Californium 36

Alpha Decay of Spheroidal Nuclei 37

Nuclear Quadrupole Resonance 38

Mass Spectroscopy 38

Double-Retarding-Field Electrostatic Beta-Ray Spectrometer. . . 41

*Previous Quarterly Reports: UCRL-2709, UCRL-2647

Space Groups 42
Structure of Indium Iodide 42

CHEMICAL ENGINEERING (PROCESS CHEMISTRY)
Notes on Work in Progress 43

GENERAL CHEMISTRY
Metals and High-Temperature Thermodynamics 44
Basic Chemistry Including Metal Chelates 45

CHEMISTRY DIVISION QUARTERLY REPORT

September, October, November 1954

Radiation Laboratory, Department of Physics
University of California, Berkeley, California

January 10, 1955

BIO-ORGANIC CHEMISTRY

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

QUANTUM REQUIREMENT IN PHOTOSYNTHESIS RELATED TO RESPIRATION

James A. Bassham and Kazuo Shibata

In the preceding report we proposed a new system, which enabled us to measure the rate of photosynthesis or the quantum requirement in photosynthesis in a straightforward way. In this system, the changes of O_2 and CO_2 in a closed system containing algae are automatically recorded by a multipoint recorder, which plots as a function of time the signals from an oxygen analyzer using the paramagnetism of O_2 and from a carbon dioxide analyzer measuring the infrared absorption by CO_2. The energy of light absorbed was observed with a bolometer, to which a sheet of opal glass was attached. The light source was a neon discharge lamp, the inside of which was coated with red pigment to prevent the transmission of any light other than nearly monochromatic red light (6300 Å).

The suspension of Chlorella pyrenoidosa (1,100 ml) was cultured with 4% CO_2 under the illumination of white fluorescent lamps. Each day, 900 ml of the culture was drawn out, and the same amount of culture medium was added to the remaining 200 ml, so that a reproducible state of culture is obtained at each harvesting, several days after inoculation. The suspension harvested was used immediately for the observation of the quantum requirement in photosynthesis. The effect of the concentration of CO_2 in air on photosynthetic rate was tested at 1% and 4%. The difference between the rates with these different concentrations of CO_2 was only a few percent, so that the photosynthetic rate under the light condition used can be considered to be saturated with respect to CO_2 with 4% CO_2. The data described below are the quantum requirement with 4% CO_2 in air.

Our purpose was to measure not only the minimum value of quantum requirement but also the change of quantum requirement with the change of the incident light intensity. With changes of the incident light intensity, we can change the ratio of photosynthesis rate against respiration, so that we can see any contribution of respiration energy to photosynthesis. In the past, there have been many discussions on the correction of quantum requirement by respiration. We observed the respiration rate during a twenty-minute period following the observation of photosynthesis. The corrected quantum requirement for photosynthesis is obtained by subtracting the dark-respiration rate from the uncorrected rate in the light. Both corrected and uncorrected values

of the quantum requirement (1/Q) are plotted against the ratio of corrected photosynthetic rate (P) and respiration rate (R). As is seen in Fig. 1, the uncorrected quantum requirement is very high at low values of P/R, which can be expected from the fact that the uncorrected quantum requirement should be infinity at compensation point (P/R=1). At high values of P/R, both uncorrected and corrected quantum requirements apparently approach a value of about 7.4. Contrary to the uncorrected value, the corrected value becomes smaller with the decrease of P/R. The lowest corrected value observed was 4.9 at P/R=1.4. If we assume that the contribution of respiration to photosynthesis continues to increase with decreasing values of P/R, the corrected quantum requirement seems to approach 4 with decreasing ratios of P/R.

In a previous report a mechanism of quantum conversion process in photosynthesis was proposed. In this theory, it was suggested that four quanta are required for producing two molecules of reducing agent with the generation of one molecule of O_2, provided enough ATP is supplied from respiration to reduce PGA. Therefore, we can expect a four-quantum requirement, if the algae respire enough to produce all the ATP required for photosynthesis. This is the case with a low value of P/R. It was proposed that, at a high value of P/R, one molecule of reducing agent must be used to produce the three molecules of ATP required for each molecule of CO_2 reduced, so that six quanta are required for the whole process, when respiration is not enough to supply all the ATP requirement. The change of quantum requirement from 4 to about 7.4 in Fig. 1 is fairly consistent with this point of view. It may be that only two molecules of ATP can be produced from the burning of one molecule of reductant, leading to a quantum requirement of seven. It is to be expected that at still higher light intensities required to obtain higher values of P/R, the light may become saturating, so that the quantum requirement may gradually rise. Thus the experimental result not only lends support to our theory, but also indicates that the correction for respiration is necessary for the estimation of quantum requirement, at least within the range of the value of P/R that we observed.

CONSTANT-DENSITY CULTURE APPARATUS FOR UNICELLULAR ALGAE

Richard E. Norris and Paul M. Hayes

In a previous report (UCRL-2531), a description was given of studies of the physiological state of Scenedesmus and Chlorella during growth which led to the design of improved apparatus to control various environmental factors. With this apparatus, it was possible to obtain steady-state conditions of growth that permitted harvests of algae with reproducible characteristics. With this apparatus, however, it is necessary to harvest a given portion of the algae at a fixed time each day in order to obtain reproducibility.

The algae culture was subjected to continuously varying light intensity during the period of growth between harvests. Studies of the quantum requirement of algae harvested at different times during this growth cycle indicated variations in photosynthetic efficiency.

In order to obtain algae cultures grown at a constant light intensity and also to permit more flexibility in harvesting, both in time and in amount, experiments have been started on the design of new apparatus. It is hoped

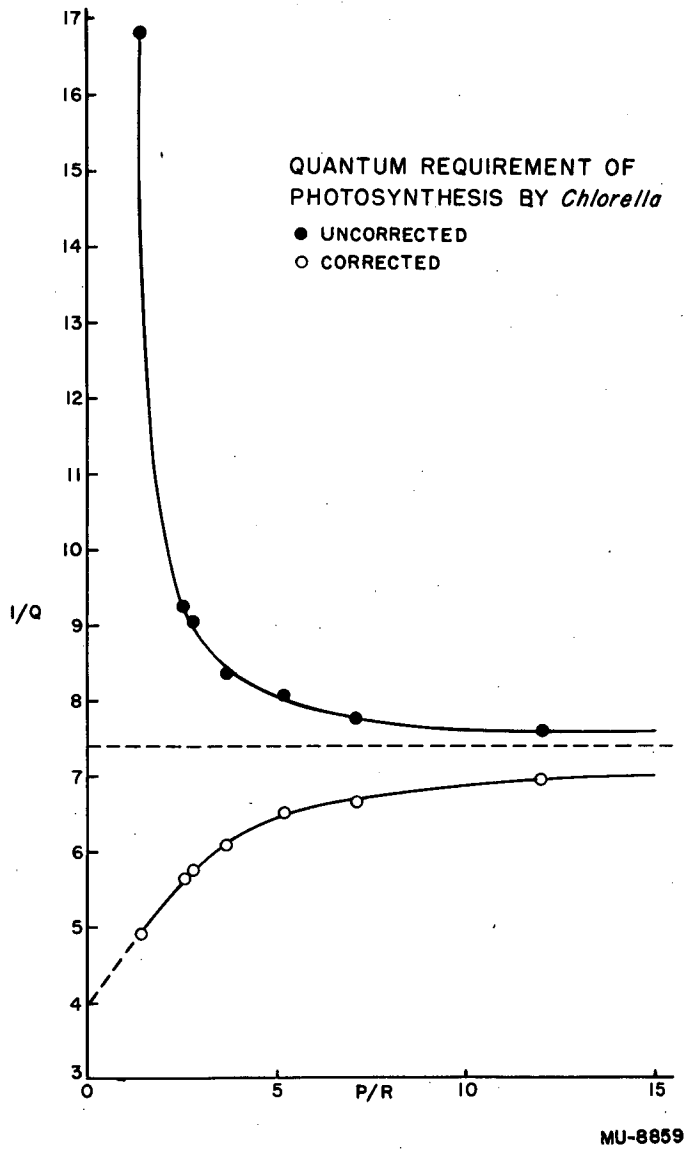
QUANTUM REQUIREMENT OF
PHOTOSYNTHESIS BY *Chlorella*
● UNCORRECTED
○ CORRECTED
1/Q
P/R
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
0
5
10
15
MU-8859

Fig. 1

that this apparatus will also lead to an increased rate of growth.

This apparatus is designed to maintain the algae suspension at a given constant density. As the algae multiply and grow the culture is diluted with new medium by means of a valve that is opened and closed by the influence of a photocell system. The photocell makes periodic readings through approximately one cm of the algae suspension. An overflow system will allow the culture to be maintained indefinitely; also, it is possible to drain from the apparatus aliquots of the algae suspension as they are needed for experimental use.

Conditions of illumination for this apparatus have been greatly improved over our present system. The improvement has been achieved by increasing the amount of light available to each culture and also by keeping the algae suspension in constant motion within a layer only 7 mm thick.

Thermostatically controlled water is continually pumped through the culture apparatus, maintaining cultures at an adjustable constant temperature.

Preliminary growth experiments with Scenedesmus in this new apparatus have given yields of approximately 1 g of wet packed cells per 100 cc of cell suspension.

STUDIES ON THE CARBOXYLATION REACTION IN PHOTOSYNTHESIS

John R. Quayle

Previous work in this laboratory with intact photosynthetic organisms and cell-free preparations of Chlorella indicated that ribulose-1, 5-diphosphate (RDP) acts as the primary carbon dioxide acceptor of photosynthesis, the RDP being carboxylated to yield phosphoglyceric acid (PGA) as the first and major reaction product.

During the past three months this carboxylation reaction in cell-free systems has been studied with particular reference to the effect of various metabolic inhibitors thereon. This work has been performed in collaboration with Dr. H. L. Kornberg. Three possible routes may be envisaged by which the carboxylation could take place:

$$(1)\quad \text{RDP} + CO_2 \xrightarrow{H_2O} 2\ \text{PGA}$$

$$(2)\quad \text{RDP} + CO_2 \xrightarrow{TPNH^+} \text{PGA} + \text{triose phosphate}$$

The $TPNH^+$ could then be regenerated by oxidation of the triose phosphate to PGA.

$$(3)\quad \text{RDP} + CO_2 \longrightarrow \text{phosphohydroxypyruvate} + \text{triose phosphate.}$$

The transformation of these products to PGA could then be linked through TPN^+ (or DPN^+) oxidation-reduction.

It was hoped that the use of certain inhibitors might permit a decision between these routes to be made, as follows. Incubation of unlabeled RDP with $NaHC^{14}O_3$ in the Chlorella extract, followed by chromatography and radio-

autography of the products, showed the major products of $C^{14}O_2$ incorporation to be phosphoglyceric acid, phosphoenol pyruvate, and malic and aspartic acids. The latter two acids undoubtedly arise from carboxylase action on pyruvic acid or phosphoenol pyruvate. Incubation of C^{14}-labeled RDP with $NaHCO_3$ in the same extract gave a large number of products arising from the over-all metabolism of the RDP, in particular, each product from the carboxylation of the diphosphate being radioactive. If an inhibitor, or combination of inhibitors, could be found that would eliminate the breakdown of RDP by routes other than the carboxylation, and also prevent the transformation

$$\text{triose phosphate} \xrightleftharpoons{DPN^+} \text{PGA},$$

then proof of the nature of the initial products of carboxylation could be obtained.

The effect of iodoacetic acid, sodium fluoride, 2,4-dinitrophenol, potassium cyanide, potassium chloromercuribenzoate, o-phenanthroline, and ATP on the fixation of $C^{14}O_2$ by RDP in the presence of Chlorella extract was studied. Their effects on PGA production can be summarized:

Table I

Compounds Showing Inhibitory Effect

Compound	Concentration	% Decrease in PGA count over control
KCN	10^{-4} M	4
KCN	10^{-3} M	44
KCN	10^{-2} M	98
K chloromercuribenzoate	10^{-3} M	92
ATP	10^{-3} M	62

Iodoacetate (10^{-2} M), NaF (10^{-2} M), 2,4-DNP (10^{-3} M) and o-phenanthroline (10^{-3} M) showed no appreciable inhibitory effect.

The inhibitory effect of KCN, K chloromercuribenzoate, and ATP have been observed by Fager[1] and, in this laboratory, by Mayaudon, both working with spinach extracts.

The effect of KCN could either be due to cyanhydrin formation with RDP, or complex formation with an essential metal factor. The action of more metal-complexing reagents is required before this question can be resolved with certainty, although it seems unlikely that there is any involvement of iron, because there is no inhibition in presence of 10^{-3} M o-phenanthroline.

[1] F. W. Fager, J. Biol. Chem. 57, 264 (1954).

It is somewhat surprising that iodoacetate shows no inhibition at 10^{-2} M concentration, in contrast to the strong inhibition of K chloromercuribenzoate. The latter effect points strongly to the participation of an-SH-containing enzyme. However, the lack of inhibition shown by iodoacetate, NaF, and 2,4-DPN was encouraging, since the former compound inhibits the triose phosphate dehydrogenase and it was hoped that the latter two would inhibit phosphatase action on RDP.

The action of these inhibitors was then studied by using C^{14}-labeled RDP and $NaHCO_3$, but certain difficulties were encountered which considerably limit the significance of the data. The results of a representative experiment are given in Table II.

A sample of the RDP-C^{14} used for the experiment was phosphatased and chromatographed, and the majority of the resulting sugar was found to be ribulose (tube No. 3, Table II). When a sample of the RDP-C^{14} was treated with previously boiled Chlorella extract and chromatographed in the usual way, it was found that a serious degree of decomposition had occurred (tube No. 4). This decomposition is partly due to the progressive decomposition of solutions of RDP on repeated freezing and thawing, and partly to its non-enzymatic decomposition during the processes preparatory to its chromatography. The results from incubation with a boiled extract, compared with those obtained from incubation with the active extract, (Tube 5), show the large error introduced at the outset of the experiments. Also, the results from any one experiment were not very reproducible (Tubes 5 and 6), indicating again the chemical instability of the RDP-C^{14}. These results do show, however, the variety of major products into which the RDP-C^{14} is metabolized.

The action of sodium iodoacetate, sodium fluoride, and 2,4-dinitrophenol, singly and in combination, was studied. Bearing in mind the errors inherent in the experiment, no significant enzymatic effect could be ascribed with any certainty to the presence of these compounds. In particular, the presence of NaF or 2,4-DPN had not noticeably diminished the phosphatasing of RDP, as evidenced by the disappearance of RDP and the appearance of sugar monophosphates. The presence of these radioactive monophosphates together with the transketolase and transaldolase systems, can provide both a source and a sink for radioactive triose phosphate. This, of course, means that the presence of radioactive triose phosphate does not have a unique significance with respect to the carboxylation of RDP.

It is clear, then, that without more efficient selective inhibitors than have yet been found, the crude extract contains too many active enzyme systems for profitable use with experiments of this type.

Table II
Studies with CO_2 and RDP-C^{14}

A. Test of carboxylating activity of extract.[1]

Tube No.	Contents	$C^{14}O_2$ incorporated into PGA
1	RM	0
2	RM + RDP	1190

B. Purity of RDP-C^{14}

Tube No.	Contents	Total counts used	Ribulose	Hexose
3	RDP-C^{14} + phosphatase	12,600	8,440	780

C. Action of extract on RDP-C^{14}, with and without inhibitors present.[2]

Tube No.	Contents	Total counts put on paper	Remaining on origin of chromatogram	Unchanged RDP	PGA	P-glycolic acid	Hexose + heptose-P	Pentose-P	Triose-P	Recovery of counts	% Recovery
4	RM* + RDP-C^{14}	23,300	2540	13,580	340	760	250**	800**	220**	18,490	79
5	RM + RDP-C^{14}	23,300	1200	12,020	665	625	1590	1480	800	18,380	79
6	Repeat of (5)	22,300	1240	9,870	800	600	1530	1130	540	15,710	70
7	RM + RDP-C^{14} + IAA (10^{-2} M)	26,200	1070	12,450	1100	980	1620	1410	720	19,350	74
8	RM + RDP-C^{14} + NaF (10^{-2} M)	25,200	1250	12,610	980	480	1580	1050	750	18,700	74
9	RM + RDP-C^{14} + 2,4-DNP(10^{-3} M)	25,900	1280	10,080	1000	600	1380	1190	510	16,100	62
10	RM + RDP-C^{14} + IAA (10^{-2} M) + NaF (10^{-2} M) + 2,4-DNP (10^{-3} M)	23,800	13,350		1350	2750		2530		19,980	84

[1] Both tubes contained the reaction mixture (RM) of 100 µl. Chlorella extract (40,000) + 40 µl. $NaHC^{14}O_3$, unlabeled RDP being added as marked. Total volume = 250 µl. Incubation time: 10 min.

[2] Each tube contained the reaction mixture (RM) of 100 µl. Chlorella extract (40,000) + 40 µl. $NaHCO_3$ solution, other substances being added as marked in the table. Total volume = 250 µl. Incubation time: 12 min. Temperature: 25°.

*Boiled extract used.

**Radioactivity in these regions, compounds not identified.

DARK FIXATION OF CO_2 BY EUGLENA

R. Clinton Fuller and E. M. Thain

The pattern of fixation of CO_2 by the plant flagellate, Euglena gracilis, was studied by this group in 1952-53. At that time it was shown that Euglena fixed CO_2 in the dark into phosphorylated compounds to a larger degree than many other algal cells. It was suggested that the pathway for the photosynthetic reduction of CO_2 was intact and functioning in the dark. With this in mind, it was decided to compare the dark-fixation products of Euglena with those of its colorless analog obtained by artificial removal of the chloroplasts by treatment with streptomycin.[1] The comparison of the dark-fixation patterns of these two forms might show a relationship between the photochemical apparatus and the enzymes concerned with the reduction of CO_2.

Upon reexamination of the dark-fixation products of Euglena with improved chromatography, the diphosphate compounds necessary for the functioning of the photosynthetic cycle could not be demonstrated in either form of the organism, and both forms appeared to have identical fixation patterns. Further evidence regarding the operation of the reduction cycle in the dark might be obtained from the distribution of radioactivity in phosphoglyceric acid isolated from the fixation products.

The phosphoglyceric acid spot was cut out from the chromatogram and treated with phosphatase, and the sample was rerun chromatographically. The active glyceric acid was eluted from the paper, mixed with crystalline calcium glycerate, and recrystallized from water-ethanol. The active salt was degraded by the method of Bassham (J. Biol. Chem. 185, 781 (1950)). Two such degradations have been carried out, in each case about 50% of the radioactivity was recovered in the barium carbonate fractions representing the carboxyl group and only traces in the dimedon derivative and barium formate--of the order of 3%. The reason for the great loss of radioactivity is being studied; but the appearance of the great preponderance of activity in the carboxyl group is an indication that this carbon is not being cycled in the normal photosynthetic reductive pathway. A possible mechanism for its formation is given in the scheme shown. This route can only lead to 1-labeled glyceric acid. It is perhaps worth noting that hexoses derived from the glyceric acid are 3, 4-labeled.

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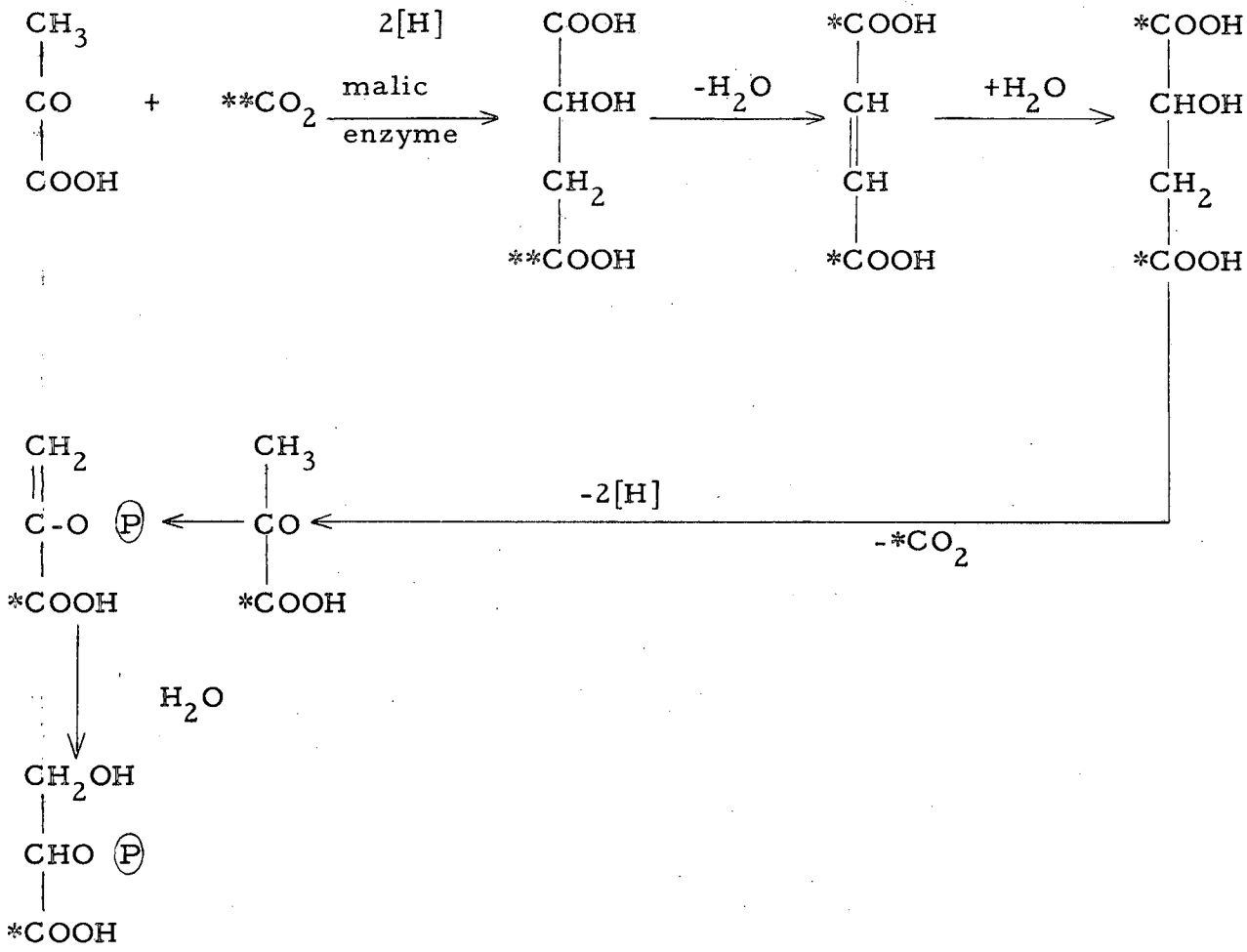
[1] L. Provasoli, S. H. Hutner, and A. Schatz, Proc. Soc. Exper. Biol. Med. 69, 279 (1948).



THE UTILIZATION OF 3-HYDROXYPYRUVIC ACID BY SCENEDESMUS

Andrew A. Benson and E. M. Thain

A study has been made of the utilization of hydroxypyruvic-2-C^{14} acid by Scenedesmus during 40 minutes in the light in the presence of air. Chromatography of an extract of the algae showed that about 60% of the radioactivity was in the glycolic acid. This compound has now been degraded by the method of Schou et al.[1] with the following radioactivity distribution results: C_1, 89%; C_2, 18%; total 107%. The quantitative recovery of the radioactivity by this degradation serves as a partial identification of glycolic acid, supplementing information derived from the paper chromatography.

It is known that the transketolase enzyme system can utilize the glycolyl group from hydroxypyruvic acid, and the results now obtained suggest that this enzyme cleaves the acid between C_1 and C_2, and that subsequent oxidation yields glycolic acid, in this instance labeled in the C_1 position, Route I. The alternative Route II to glycolic acid, via the decarboxylation of the tautomers of hydroxypyruvic acid (tartronic semialdehyde), now seems improbable. This would lead to 1-and-2-labeled glycolic acid via route II.

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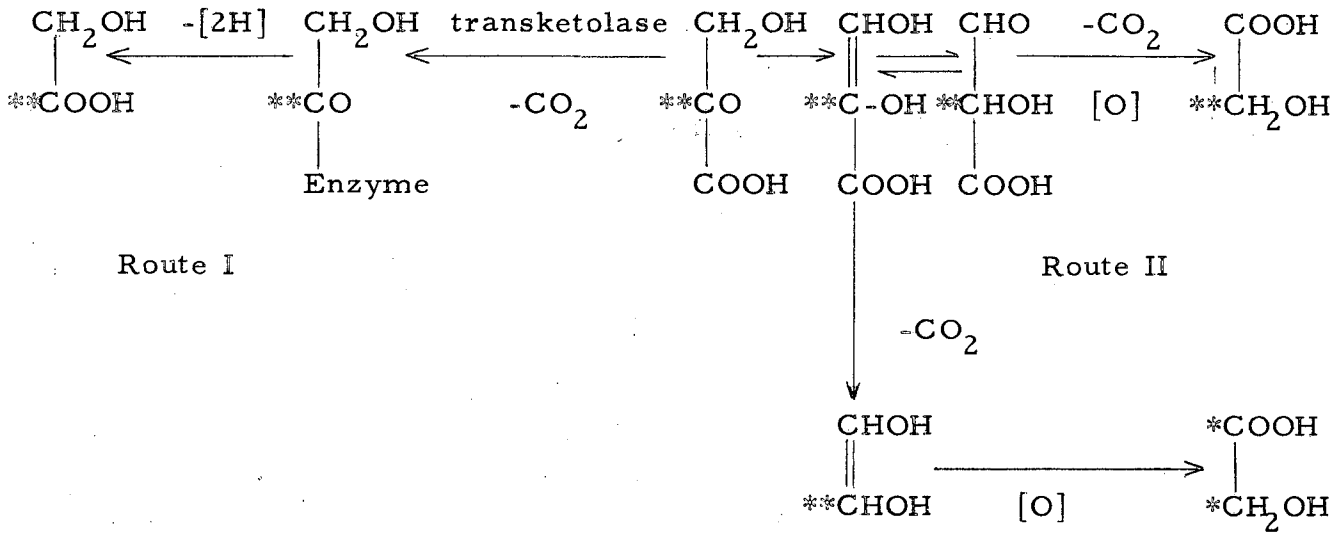
[1] L. Schou, A. A. Benson, J. A. Bassham, and M. Calvin, Physiol. Planta. 3, 487 (1950).



The glycolic acid, then, is derived by oxidation of the glycolyl transketolase (enzyme) intermediate.

BRAIN CHOLINESTERASE AND ADJUSTIVE BEHAVIOR PATTERNS

Edward L. Bennett, Barbara Krueckel, and Alvin Halevy

The cooperative investigation--with Professors David Krech and Mark R. Rosenzweig of the Department of Psychology, University of California--of the metabolism of brain and the adjustive behavioral patterns of the rat has been continued (UCRL-2709). During the past 3 months, an additional 23 male rats have been analyzed for the cholinesterase pattern of the cortex as was described previously. The correlation of the distribution of cholinesterase concentration with behavioral patterns, which was found with the first 20 rats studied, has been confirmed with these additional rats. In addition, it appears that further correlations of hemispheric dominance, cholinesterase, and behavior may be found with the additional data now available.

The analyses are being extended to female rats, but at the present time not enough rats have been analyzed to permit any conclusions.

Initial attempts to analyze the cortex for coenzyme A content have indicated that the amount present is too small to be quantitatively determined with the present procedure, but it is expected that suitable modifications of the analytical method will enable us to make these analyses.

AN INSTRUMENT FOR CONTINUOUS MEASUREMENT OF BREATH-$C^{14}O_2$ METABOLISM RATES IN HUMANS

B. M. Tolbert, Martha Kirk, and Elton M. Baker

In an earlier Quarterly Report (UCRL-2531) an instrument was described which permitted continuous analysis of the respiratory carbon dioxide from small experimental animals that had been given doses of various radioactive compounds. This instrument continuously measures respiratory C^{14}, CO_2,

and the ratio between the two (i.e. C^{14}/CO_2), and records the results on a multichannel analyzer. A leter report (UCRL-2709) describes the solutions to some of the problems that have arisen with this instrument.

The next step was to expand the apparatus to include human studies. This has presented some interesting and challenging problems. Since an adult at rest breathes in and out about seven liters of air per minute and the CO_2 content of the expired air is about 4%, a flow rate of ten liters per minute should provide sufficient O_2 and maintain the CO_2 content of the air passing through the system at about 2 to 2.5%.

To accommodate such a flow rate an ion chamber with a volume of ten liters was designed. As originally constructed, the chamber was made of brass and chromium plated on the inside. The probe of stainless steel was designed to go the full length of the chamber, being fastened to the regular insulator assembly on one end and fitting into another insulator at the top of the chamber. Both these insulators were made of teflon. This design proved to have quite a high and variable background, with an α-count of more than 3 per minute. Furthermore, the chamber was quite sensitive to flow rate. A copper wire mesh screen grid, or cage, such as described in the preceeding report (UCRL-2709), reduced the background and α-count only in proportion to the reduction in the effective volume of the chamber. The use of stainless steel mesh in the place of copper reduced much better the number of α's recorded.

In an attempt to combat this problem of flow sensitivity, an ion trap was made of two concentric stainless steel tubes two feet long. These were insulated from each other and a potential of 300 volts was impressed on them. The air on its way to the ion chamber was passed between these tubes, which were highly polished on the adjacent surfaces. Results were disappointing; no change was produced in the background or flow characteristics. Flow sensitivity was finally entirely overcome by dispensing with the top insulator and using a sapphire insulator in the bottom assembly. It is presumed that air currents over the teflon insulators had been responsible--an interesting effect.

Chamber background, however, was still rather high and variable, and the average α-count was between 1.5 and 2 per minute. Various types of air filters were tried, none of which was helpful. It was shown, however, that the H_2SO_4 bubbler and glass wool plug that had been included in the flow system for drying purposes were also helping to clean the air entering the chamber.

Because it was realized that many of our background problems might arise from contamination of room air by radon, thoron, etc. from the concrete walls and other sources about us, the use of air from compressed air cylinders that had been stored long enough for these contaminants to decay was suggested as a possible solution. Results were very good; both the background and α-count rate were reduced to acceptable values.

The chamber was calibrated as usual, by filling with a $C^{14}O_2$-plus-air mixture of known radioactivity and recording the current produced.

Finally, with a flow rate of 10 liters per minute of air from the compressed-air cylinder, through the H_2SO_4 bubbler and glass wool plug into the

ion chamber fitted with stainless steel screen and sapphire insulator, a very uniform background was obtained, equivalent to $1.07 \pm 0.05 \times 10^{-3}$ μc of C^{14} and averaging 1 α-pulse every two minutes. Having a patient in the line raised the background by about 6×10^{-5} μc C^{14}.

Thus, if the most sensitive resistor is used, it should be possible to accurately measure breath radioactivity equal to no more than one half of the background value. In other words, since air in the ion chamber is turning over once per minute, one should be able to make quite accurate measurement of breath C^{14} as low as 5×10^{-4} μc per minute.

An investigation of commercially available face masks or helmets showed none that was easily sealed or comfortable for a period of hours. Consequently, we have had constructed a helmet of 1/16-inch lucite large enough to fit over the head, and shaped to fit the shoulders, chest, and back. To assure complete sealing and comfortable fit around the shoulders, a piece of 1-inch sponge rubber large enough to form a shawl was fastened to the lucite and secured with a strap which passes under the arms and across the chest and back of the patient. Two holes in front of the helmet at about nose and mouth level provide for air inlet connections from the compressed-air cylinder, and the outlet is placed on the side of the helmet. Thus, the helmet may be worn quite comfortably whether the patient is standing, sitting, or lying down.

As finally set up, the flow system for human experiments is as follows: Air flows from an air cylinder, through a rotameter of suitable capacity, through the helmet, H_2SO_4 trap, and glass wool, and into the ion chamber. After passing through the chamber about 100 ml/min is diverted, by means of a small pump, through the CO_2 analyzer. Most of the air, however, continues through another rotameter, a wet-test meter, and a soda-lime tube before being exhausted into the room.

RESPIRATORY METABOLISM OF LABELED ORGANIC COMPOUNDS

Ann M. Hughes, Martha R. Kirk, and B. M. Tolbert

Partial analysis of a group of metabolism rate curves from animals injected with various C^{14}-labeled compounds was given in a previous report (UCRL-2647). At present these rate studies have been extended to include glyceryl-tripalmitate-1-C_3^{14} in rats, and experiments in which the C^{14} content of the injected sodium acetate-2-C^{14} was varied by a tenfold factor to demonstrate the comparative accuracy of the instrument at different activity levels. Results of these experiments are shown in Table III The delay in the specific activity maximum in the animals that received the small amount of activity is equivalent to the difference in time constant of the resistors used in the two sets of experiments.

As a continuation of the studies on the effect of substrate concentration on the $C^{14}O_2$ metabolism of acetate in PAD rats reported last quarter, the experiments were repeated, using pantothenic-acid-deficient (PAD) rats instead of normal ones. The total amount of acetate was varied from 0.2 mg to 20 mg, keeping the radioactivity constant at 5μc sodium acetate-2-C^{14}. The total volume of solution injected was always 0.1 ml. The apparatus for measuring $C^{14}O_2$ respiration has been previously described (UCRL-2531).

As in the previous report on normal animals, these experiments on PAD rats showed no significant differences in the $C^{14}O_2$ recovery over the substrate concentration range studied. These data show that in the range of 0.2 to 20 mg Na acetate the rate of excretion of radioactivity is not a function of dose size, and thus show that flooding of the system does not occur.

Table III

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

Glyceryl-tripalmitate-1-C^{14} (Average of 3 rats)

Total % Recovery of Injected Activity	Times of Peak Specific Activities
8 hours after inj. 7.60% 48 " " " 38.16%	87 min, 7 hr, 29 hr, 54 hr

Sodium acetate-2-C^{14} (Average of 2 rats each)

Injected Dose	Total Recovery in 7 hours	Time of Maximum Specific Activity
1.34 μc	66.12%	35 min.
12.00 μc	60.33%	27 min.

THE ACUTE EFFECT OF NICOTINE ON THE METABOLISM TO $C^{14}O_2$ OF ACETATE IN NORMAL RATS

Ann M. Hughes, John Weaver, and B. M. Tolbert

The literature on the pharmacology of nicotine contains very few references to metabolic studies. Smith et al.[1] injected nicotine daily into young rats, and reported normal growth but depletion of total body fat after several months. In vitro measurement (manometrically) of the respiration of brain, kidney, and liver slices of rats injected daily with nicotine for 60 to 100 days showed inhibition of brain and kidney respiration, and increase of liver respiration.[2] The metabolism of ascites tumor is also inhibited by nicotine.[3] Our apparatus for measuring $C^{14}O_2$ respiration in small animals (UCRL-2531) provides a simple method for studying the in vivo respiratory effects of nicotine.

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[1] C. S. Smith et al, , J. Pharmacol. 55:274, 1953.

[2] I. Yamamoto and Y. Kurogochi, Folia Pharmacol. Japon. 47, No. 2, Proc. 50-1 (1951).

[3] H. Schmitz, Z. Krebsforsch. 57, 405 (1951).

Young Long-Evans rats (50 to 75 g) were used. In the first series of experiments, the concentration of nicotine was 0.04 mg/100 g body weight. In the second series, the nicotine dosage was increased to 0.1 mg/100 g body weight. In all the experiments the acetate dose was 2 mg (about 5 μc sodium acetate-2-C^{14}). All injections were intraperitoneal, the nicotine preceding the acetate by about 10 seconds.

In the series in which the nicotine dosage was 0.04 mg there was no change in $C^{14}O_2$ recovery. In the series in which the nicotine dosage was 0.1 mg there was a slight depression of $C^{14}O_2$ respiration, which was probably due to the respiratory irregularities caused by the high nicotine concentration; i.e., during the first 5 to 10 minutes after injection, the rats' respiration was gasping and spasmodic, after which it returned to normal.

Experiments have also been started to study the chronic effects of nicotine on acetate metabolism. Starting on the day of weaning, rats are being injected daily with 0.1 mg/100 g body weight nicotine subcutaneously. It is planned to compare their metabolism of acetate with that of normal litter-mate rats at weekly intervals.

A LIQUID SCINTILLATION COUNTER FOR TRITIUM MEASUREMENT

Elton M. Baker

Most successful methods for the measurement of low-energy β-particle detection involve an internal gas counter tube, in which the counting efficiency is high because of the efficient absorption of the energy of the β-particle. The improvement of the photomultiplier tube, together with increasing information concerning the fluorescence effects due to absorption of radiation in organic crystals and solutions, has made it possible to develop an efficient method for the detection of tritium in some organic compounds and in water. The elimination of the combustion of organic compounds to obtain a tritiated water sample from which hydrogen or other gases, such as methane, may be generated, in conjunction with a vibrating reed electrometer or a proportional counter has made the detection process simpler for organic compounds containing a benzene ring. Carboxylated, halogenated, nitro- and sulfur-containing compounds interfere with the light-emission properties of presently known fluorescent compounds, so must of necessity be avoided. Furthermore, the compounds containing tritium must be completely soluble in solvents such as toluene and xylene and form clear solutions at low temperatures.

The use of liquid-scintillation counters as a method for measuring low-energy radiation has been shown to be satisfactory by recent workers,[1] who have adapted counters designed for measuring hard gamma radiation to the counting of tritium and C^{14}. Much of this work has centered around the use of photomultiplier tubes coupled to vials containing the liquid scintillator and the radioactive compounds. For tritium or C^{14} the energy from the emitted β-particle is quite low, and light emission is correspondingly low, and any satisfactory counting efficiency must therefore be obtained by operating the photomultiplier tubes at high voltage between the photocathode and the first dynode so as to have the highest amplification with the minimum tube noise. The method of improvement of counting efficiency proposed here is to operate

[1] D. J. Rosenthal and H. O. Anger, Rev. Sci. Instr. 25, 670 (1954).

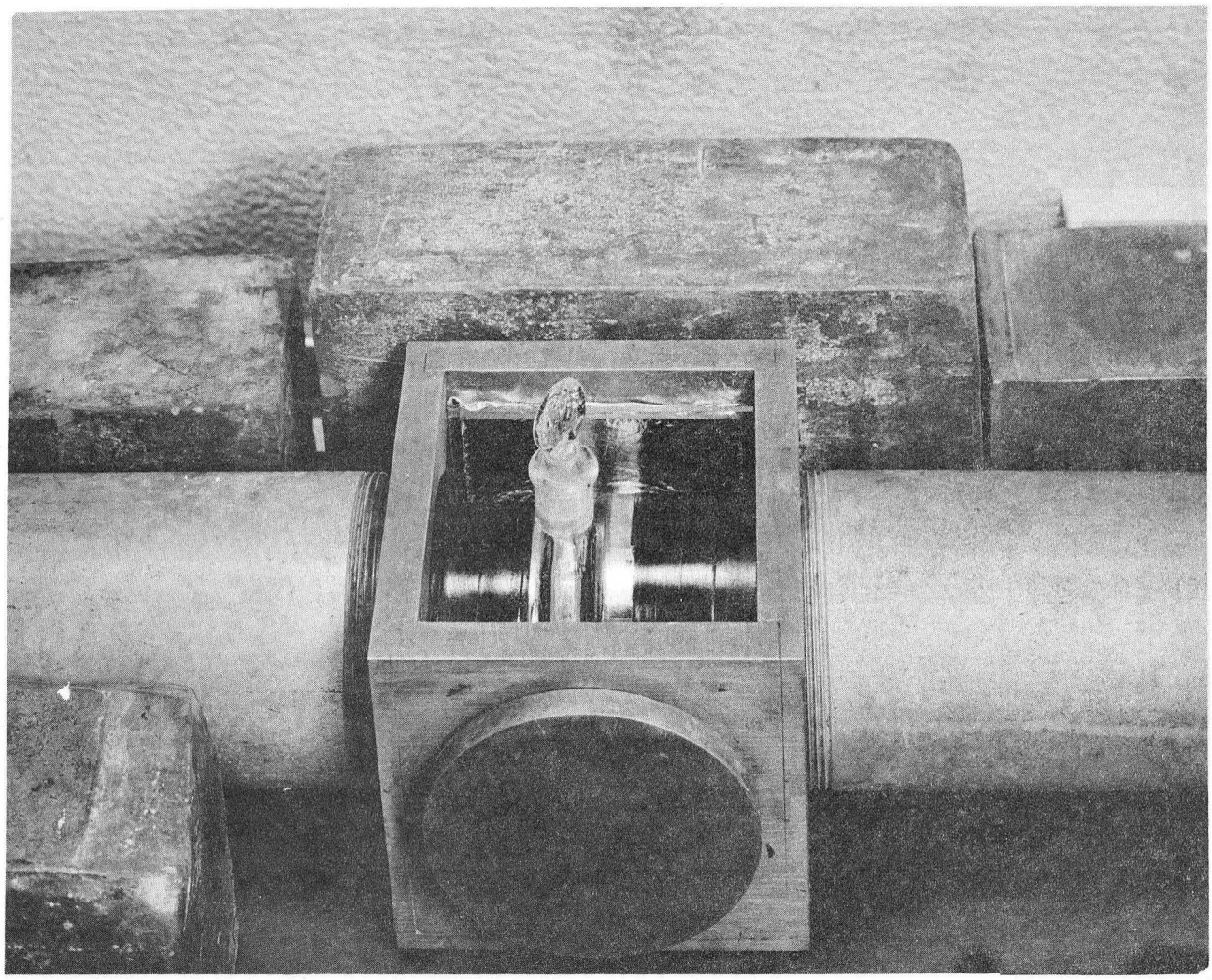
two or three photomultiplier tubes arranged to give the highest possible light-collection efficiency. This latter is dependent upon the ratio of liquid-scintillator surface area to photocathode area, the absorption of light by the scintillator and glass container, and the degree of reflectivity of light from the walls of the vessel.

Apparatus

The apparatus, Fig. 2, consists of a brass lighttight box with openings available on three sides and the bottom. With a box of such wide versatility, two photomultiplier tubes may be mounted so that the photocathodes are facing each other or at right angles to each other, and if three tubes are used they may be placed at right angles to each other. It has been observed (UCRL-2633) that the arrangement of the tubes makes only a slight increase in the background which is not easily reduced as long as a photomultiplier tube may be "seen" by another photomultiplier tube. The distance between the tubes may be adjusted so as to accommodate vessels of various thicknesses containing the liquid-scintillator solution. The photomultiplier tubes are optically sealed to the vessel by means of a clear high-viscosity silicone fluid (DC 200 Silicone fluid, viscosity 1,000,000 centistokes; Dow-Corning Corp., Midland, Michigan), which has a minimum absorption of light. The vessels containing the radioactive sample and the scintillator are flat, and thin, circular when mounted between two tubes and three-sided when three tubes are used.

A series resistor system with components chosen so that the voltage across the photocathode and first dynode is 150 volts, with 100 volts across the other dynodes, is bridged across the photomultiplier tube. This arrangement allows for efficient collection of the electrons on the first dynode without too great effects of saturation between the last dynode and anodes when the total voltage is increased across the system. The signal is taken from the second dynode to the grid of the first of two 6AK5 tubes as amplifiers and one 6AK5 tube as a cathode follower, mounted as close as possible to the base of the photomultiplier tubes. The photomultiplier tubes and preamplifier system are shielded in an iron cylinder surrounded by two inches of lead. This portion of the system is contained in a General Electric Model 7 freezing unit, with temperature controlled at -17°C. The preamplifiers are then connected by a shielded cable to the coincidence unit.

The coincidence circuit is arranged so that the voltage pulse from the preamplifier triggers the scaler amplifier system if the light producing the pulse in the first photomultiplier tube also produces a pulse simultaneously in the second photomultiplier tube. The amplifier gain is 3,000 and that of the photomultiplier tube is approximately 10^6. The circuit allows counting to take place if the two pulses produced by the same fluorescence are not separated in time by more than 2 microseconds. The maximum dead time under normal operation of the response of the coincidence circuit is provided so that excessive noise may be eliminated (this, however, prevents some of the low-energy β-particles from being counted). The excessively large pulses from external radiation sources such as μ-mesons are removed by an anti-coincidence discriminator. This reduces the background count by approximately one-fourth. A block diagram, Fig. 3, shows the general arrangement of apparatus.



ZN-1151

Fig. 2. Flat sample holder viewed by two photomultiplier tubes in lighttight box.

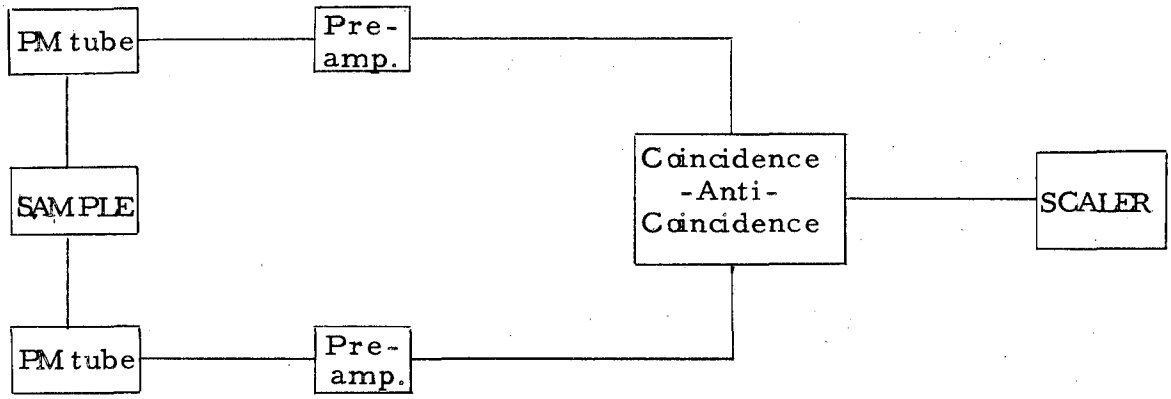


Fig. 3. Block diagram showing connection of units for counting of tritium.

Materials

The scintillation solution consists of 5.0 g of diphenyloxazole as the principal scintillation solute and 30 mg of alpha-naphthylphenyloxazole as the spectrum shifter (fluorescence maximum, 4050 Å) dissolved in 1,000 g of freshly distilled water-free toluene.

The emission spectrum of the solution is characteristic of the alpha-napthylphenyloxazole. Its emission maximum is close to the sensitive peak of the photomultiplier tube, i.e. near 4800 Å.

Tritiated benzoic acid was made by heating benzoic acid with concentrated T-sulfuric acid at 100° C for 24 hours. The undecomposed acid was dissolved in NaOH solution, precipitated with HCl, filtered, and dried. The product was further purified by recrystallization from diethylether. The ring-labeled tritium-containing compound was converted to water by combustion and the water was analyzed for tritium by filling an ion chamber with the hydrogen gas produced by the reaction of the water with $LiAlH_4$ diethylcarbitol solution in a closed evacuated system.

Results and Discussion

The photomultiplier tubes operated at -17° C have a low cesium vapor pressure. The low temperature and the resulting low vapor pressure decreases the number of extraneous particles that hit the photocathode and cause electrons to be ejected and amplified as "dark current" noise. This noise is further reduced from 6,000 counts per minute to 50 counts per minute by counting only those few noise pulses which accidentally appear within 2 microseconds in each of two photomultiplier tubes when operated at 1,500 volts between the photocathode and final dynode. The noise background increases somewhat with voltage across the dynodes. At 1,300 volts there are 9 counts per minute and at 1,600 volts there are 220 counts per minute for two tubes in coincidence. At the higher voltage the noise in each individual tube is too great to give satisfactory precision. The noise counts are so great in number that they can possibly cause a saturation of the amplification system and create a greater

dead time with less resolution of the counts due to radioactivity. If three tubes are used in coincidence, noise may be reduced from 200,000 counts per minute to 100 counts per minute at 1,800 volts across the cathode and last dynode. When three photomultiplier tubes are used, however, they cannot be placed any closer together than in a triangle formed by the faces of three tubes. This results in greater absorption of the light before it reaches the photocathode surface, as well as inefficient light reflection. The best efficiency is obtained with two photomultiplier tubes arranged so that the distance between the photocathode surfaces is at the minimum and the light therefore travels the shortest possible distance. A vessel with diameter not greater than that of the photocathode allows the tube to "see" a larger percentage of the scintillation solution area. The area of phosphor that is not facing either one of the photocathodes is then at a minimum, and loss due to light's escaping the scintillator is extremely small. However, the maximum light to affect the photocathode of either of the two photomultiplier tubes is less than half of the light produced by a single scintillation. This one factor is the greatest disadvantage of the system because the low-energy particles from tritium have less than 5 kev. The amount of light reaching both tubes is reduced to a value lower than that necessary to cause the electrons to be ejected from both cathodes simultaneously. The efficiency of conversion of energy to photons is not more than 10%. The resulting counts then are due to a probable effective 3 or 4% of the original energy at most.

It was found that the most efficient method of counting tritium samples was obtained in a flat "pancake"-shaped vessel with two photomultiplier tubes facing each other and separated by the shortest distance convenient to construct, namely, a vessel 6 mm thick and 45 mm in diameter. As shown in Table IV, an increase in the thickness or the diameter of the vessel provides a larger volume of phosphor and therefore allows more light loss by absorption in the phosphor solution as well as an increase in the absorption of light by the larger surfaces adjacent to the photocathode surface. The low ratio of photocathode surface area to vessel surface area decreases the efficiency of light collection. Also, the background increases proportionately as the volume of the scintillator, because more external radiation is collected in the scintillator or because of radiation impurities in the solution.

Table IV

Counting efficiency vs. type of containing vessel for scintillator

Volume (ml)	Distance between PM tubes	Background noise and scintillator (cpm)	Tritium sample (32600 d/m)	Efficiency (%)
1.6	6 mm	218	14156	43.4
4.6	7 mm	249	12121	37.2
9.0	8 mm	636	11650	35.7
9.5	cylinder	238	3794	11.6

In summary: The arrangement using two tubes in coincidence is superior to three tubes in coincidence, and provides greater counting efficiency of β-particle from tritium, since the gain in the photomultiplier tube accomplished by using a higher voltage across the photocathode and last dynode, and the

decreased noise background in the latter, are somewhat nullified by the necessary arrangement of three tubes which does not allow a high ratio of solution surface to photocathode surface as with the pancake-shaped vessel between two photomultiplier tubes.

Table IV shows a comparison of size of vessels and counting efficiency of the toluene-diphenyloxazole-alphanaphthylphenyloxazole solution containing tritiated benzoic acid. Samples placed in the flat vessel between two photomultiplier tubes show a marked increase in counting efficiency owing to decreased light loss, as light passes through a very short distance before reaching the photocathode surface. Samples used in the scintillator were 40 micrograms, so the effects due to quenching were reduced to a minimum. All samples were compared with that of a sample of water obtained from Los Alamos Scientific Laboratory by ion chamber methods.

Table V shows the change in counting efficiency with increase in voltage across the photocathode and last dynode. The background noise in the photomultiplier tubes remain at a very low value as compared with the single tube value.

The counting efficiency of tritium is less than it would be for C^{14}, since the average energy of the β-particle is eight times greater than that for tritium.

Table V

Counting efficiency vs. voltage across cathode and last dynode

Voltage on PM tubes	Background Noise (cpm)	Background Noise + cosmic (cpm)	Sample (d/m)	Efficiency (%)
1400	16	90	6368	19.5
1500	34	115	10240	31.4
1600	84	218	14156	43.4
1700	150	282	16948	51.9
1750	199	333	18048	55.4

A PYRROLIDINE REARRANGEMENT

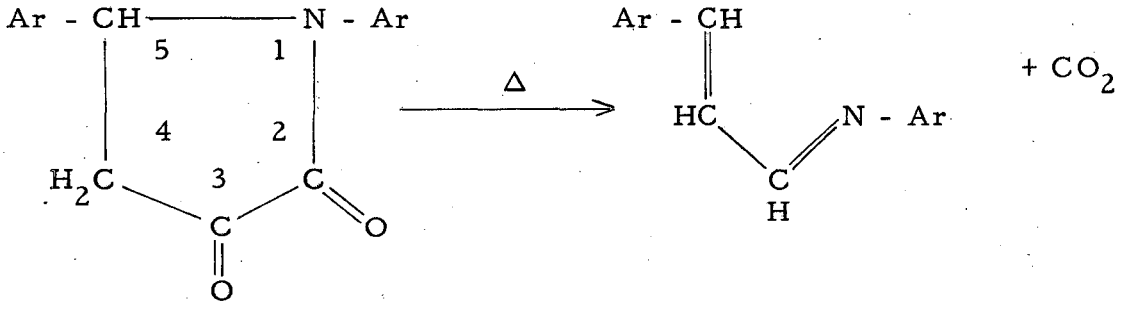
Hans Grisebach

The observation that 1,5-diaryl-2,3-pyrrolidinediones (I) evolve carbon dioxide upon thermal decomposition was first reported by Johnson and Adams.[1] Later Vaughan and Peters[2] made an intensive study of the reaction and identi-

[1] J. R. Johnson and R. Adams, J. Am. Chem. Soc. 45, 1307 (1923).

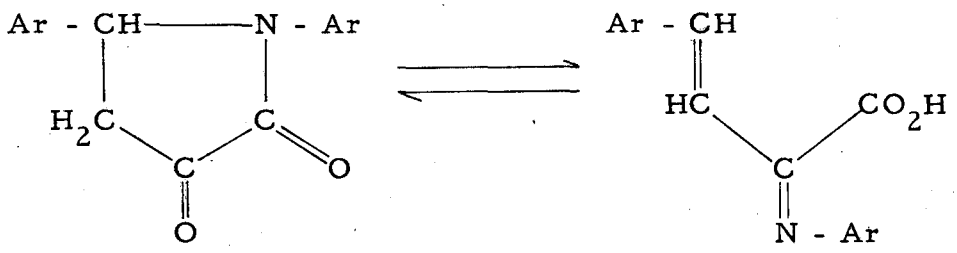
[2] W. R. Vaughan and L. R. Peters, J. Org. Chem. 18, 382 (1953).

fied the other decomposition product as a cinnamylideneaniline (III).



I III

Furthermore, Vaughan and Peters showed that the 1,5-diaryl-2,3-pyrrolidinediones are in equilibrium with the corresponding 2-arylamino-3-benzylidenepropionic acids (II).



II

From kinetic measurements, uv spectra, and conductance data the authors concluded that the decarboxylation of (I) proceeds via (II) and that the decarboxylation of (II) is the rate-determining step of the reaction (cf. UCRL-2647, p. 41-43).

$$\mathrm{I} \underset{\text{fast}}{\rightleftharpoons} \mathrm{II} \xrightarrow[\text{slow}]{} \mathrm{III} + CO_2$$

In a search for more information about this unusual reaction, the decarboxylation was studied with 1-(4-nitrophenyl)-5-phenyl-2,3-pyrrolidinedione-3-C^{14}, (IV). The labeled pyrrolidinedione was prepared according to the procedure of Borsche[3] from pyruvic acid-2-C^{14}, benzaldehyde, and p-nitroaniline. The pure (IV) was decarboxylated by heating for 8 hours in boiling o-dichlorobenzene. The carbon dioxide evolved was swept with a stream of nitrogen into a trap with sodium hydroxide. At the end of the reaction the decomposition product N-cinnamylidene-p-nitroaniline (V) was isolated and the purified (V) was combusted according to Van Slyke to carbon dioxide. The specific radioactivity

[3] W. Borsche, Ber. deut. chem. Ges. 41, 3884 (1908).

of the $BaCO_3$ from the carbon dioxide evolved during the decarboxylation was only 0.11% of the radioactivity of the $BaCO_3$ from (IV) or (V). Thus it is shown that the evolved CO_2 comes only from Position 2 of the pyrrolidinedione and no rearrangement of the carbon skeleton takes place during the decarboxylation.

To see if the rearrangement from (I) to (II) is intra- or intermolecular, this rearrangement was further investigated in the presence of labeled p-anisidine. The labeled p-anisidine was prepared by methylation of silver p-nitrophenolate with $C^{14}H_3I$ followed by reduction to the p-anisidine-C^{14}. By heating a suspension of 3-anisilydene-2-(4-methoxyphenylimino)propionic acid in a methanolic solution of the radioactive p-anisidine for one minute in a steam bath (conditions for the rearrangement of the corresponding pyrrolidinedione to the acid) it was found that a rapid exchange took place between the p-anisidine residue of the acid and the p-anisidine in solution. After recrystallization to constant radioactivity the exchange was 51% (related to 100% of the theoretical exchange). Therefore, the rearrangement from (I) to (II) could not be investigated with this method. The result only shows that the p-anisidine residue in the acid is very labile under the conditions of the rearrangement.

Experimental

Thermal decomposition. A solution of 296 mg (1 mmole) of (IV) in 60 ml o-dichlorobenzene was refluxed 8 hours under nitrogen. The evolved carbon dioxide was swept with nitrogen into a trap containing 50 ml 1% carbonate-free sodium hydroxide. The dichlorobenzene was distilled off under N_2 at 30 mm, leaving the N-cinnamylidine-p-nitroaniline as a yellow residue which was recrystallized from acetonitrile (ca 1.5 ml) and from abs. ethanol; mp 122°-124°.

Radioactive measurements. Barium carbonate from pyrrolidinedione, 32,700 cpm/mg; barium carbonate from cinnamylideneaniline, 33,000 cpm/mg; barium carbonate from thermal decomposition, 37 cpm/mg.

p-Anisidine-C^{14}. A suspension of 738 mg silver p-nitrophenolate (dried in vacuo over P_2O_5) in 0.19 ml $C^{14}H_3I$ and 10 ml abs. ether was stirred for 15 hours. After the silver iodide was filtered and washed with ether, the ether was extracted with 2 N sodium carbonate and washed with water. The dry ethereal solution was evaporated, leaving yellow crystals of p-nitrophenol, mp 46°, yield 430 mg (93.5%). The crude product was dissolved in ethanol and hydrogenated with PtO_2/H_2. The p-anisidine was recrystallized from petrol ether.

Exchange between p-anisidine-C^{14} and 3-anisilydene-2-(4-methoxy-phenylimino)-propionic acid. On a steam bath, 100 mg acid (0.321 mmole), 5 mg p-anisidine (0.0407 mmole), and 5 ml abs. methanol were heated for one minute. The suspension was then cooled rapidly, and the acid was filtered and washed several times with hot methanol. The acid was recrystallized 4 times from methanol; mp 155°, mixed melting point with the original acid was not depressed. A part of the acid was rearranged to the corresponding pyrrolidinedione by recrystallization from boiling ethanol-acetic acid (8:1 vol). The pyrrolidinedione showed the same radioactivity as the acid.

THE SYNTHESIS OF DL-THIOCTIC ACID

Patricia T. Adams

DL-thioctic acid (DL-α-lipoic acid) has been prepared by the following procedure (Lester J. Reed and C. Niu, J. Am. Chem. Soc., in press). Ethyl 5-chloroformylvalerate was prepared by the method of E. Blaise and L. Koehler.[1] Treatment with two moles of aluminum chloride and excess ethylene in carbon tetrachloride solution transformed this acid chloride into ethyl 6-keto-8-chloro octanoate. Distillation at reduced pressure resulted in the loss of hydrogen chloride to give ethyl 6-keto-7-octenoate in 70% yield from the acid chloride. The vinyl ketone was treated with gaseous hydrogen bromide at 0° C, followed by reduction with sodium borohydride to form 6-hydroxy-8-bromo octanoate in 55% yield.

The hydroxy ester was converted to ethyl 6, 8-dibromooctanoate with phosphorus tribromide in carbon tetrachloride solution in the cold. The yield to the dibromide was 50%. The 6, 8-dibromo ester was redistilled for analysis; bp $115^{\circ}-16^{\circ}$ (0.2 mm); n_D^{25} 1.4940. Analysis: calc'd for $C_{10}H_{18}O_2Br_2$: C, 36.39; H, 5.50; Br, 48.42; found: C, 36.31; H, 5.55; Br, 48.1.

6, 8-dibenzylmercapto octanoic acid was prepared by treatment of the dibromoester with sodium benzylmercaptide in ethanol, followed by alkaline hydrolysis. The crude product was recrystallized from benzene-hexane to yield 50% of white crystals. Reduction of this compound with sodium in liquid ammonia, followed by oxidation of the dithiol in aqueous (pH 7-8) solution with ferric chloride catalysis, gave a viscous yellow oil. The product was extracted into hot hexane, allowed to crystallize, isolated, and recrystallized from hexane. DL-thioctic acid was isolated in large, light yellow platelets, mp (uncorr.) $59^{\circ}-60^{\circ}$. The yield from dibenzylmercapto ester was 60%. This sample showed the characteristic ultraviolet absorption spectrum with λ_{min}, 280 mμ; λ_{max}, 333 mμ; ϵ_{max}, 149. Analysis: calc'd for $C_8H_{14}O_2S_2$: C, 46.57; H, 6.84; S, 31.08; found: C, 46.65; H, 6.72; S, 30.86.

LEUCYLALANINE-2-C^{14}

Rosemarie Ostwald

L-Leucyl-D, L-alanine-2-C^{14} was prepared from sodium propionate-2-C^{14} by the following sequence of steps:

$$CH_3\overset{*}{C}H_2COONa \longrightarrow CH_3\overset{*}{C}H_2COOH \longrightarrow CH_3\overset{*}{C}HBrCOOH \longrightarrow CH_3\overset{*}{C}H(NH_2)COOH$$

sodium propionate — propionic acid — bromo-propionic acid — alanine

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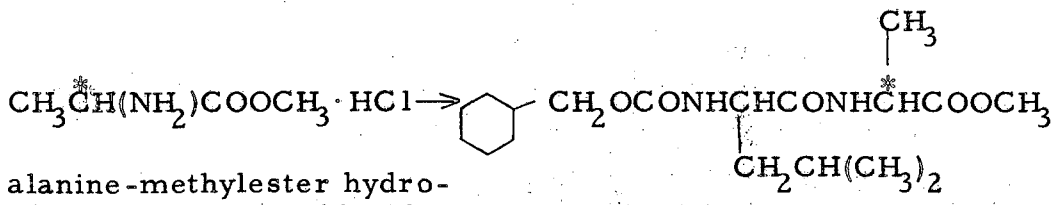
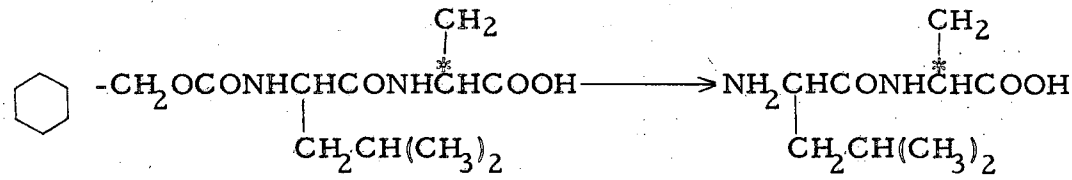
[1] Bull soc. chim. [4] 7, 219 (1910).



alanine-methylester hydrochloride

carbobenzoxy-L-leucyl-D, L-alanine-methylester



carbobenzoxy-L-leucyl-D, L-alanine L-leucyl-D, L-alanine

The procedures used have been described in J. Am. Chem. Soc. 74, 2435 (1952) and UCRL-2455 and UCRL-2647.

The preparation was performed in two batches. The yields were as follows: (1) 16.8 mM sodium propionate (16.8 mc) $\xrightarrow{52\%}$ 13 mM alanine (8.6 mc) $\xrightarrow{70\%}$ 9.4 mM alaninemethylester hydrochloride (6 mc) $\xrightarrow{21\%}$ 1.9 mM carbobenzoxy-leucyl-alanineester (1.3 mc) $\xrightarrow{75\%}$ 1.6 mM crude leucyl-alanine (0.94 mc). The over-all yield from sodium propionate to crude leucyl-alanine was 5.7%, and 0.6 mc was recovered as alanine, representing 3.5% of the starting activity. (2) 13.7 mM sodium propionate (13.7 mc) $\xrightarrow{79\%}$ 15 mM alanine (10.8 mc) $\xrightarrow{76\%}$ 16.2 mM alaninemethylester hydrochloride (8.2 mc $\xrightarrow{72\%}$ 8.5 mM carbobenzoxy-leucyl-alanineester (6 mc) $\xrightarrow{79\%}$ 9.3 mM crude leucyl-alanine (4.8 mc). The over-all yield from sodium propionate to crude leucyl-alanine was 35%, and 3.2 mc was recovered as alanine, representing 23% of the starting activity.

The peptide so obtained was not pure. Its major contaminant was about 50% of a radioactive compound which was identified as an inter- or intramolecular anhydride by its chromatographic behaviour on paper and ion exchange columns, and by cochromatography with synthetic leucyl-alanine anhydride. It was formed during the hydrogenation of carbobenzoxy-leucyl-alanine from carbobenzoxy-leucyl-alanine ester which had remained unsaponified in the preceding step.

The mixture of leucyl-alanine and leucyl-alanine anhydride can be separated by either a cation or anion exchanger. Phenol has to be avoided as chromatographic solvent, because the pure peptide has been found to form the anhydride under these conditions.

EFFECTS OF IONIZING RADIATION ON CHOLINE CHLORIDE AND ITS ANALOGS

Richard M. Lemmon and Margaret A. Parsons

The program of determining the effects of changes in the choline chloride molecule on radiation sensitivity (UCRL-2647) is being continued. In Table VI are listed the results obtained on the radiation decomposition of choline chloride analogs since the earlier report. The irradiation procedures and analytical techniques are the same.

In addition to the experiments of which the results are listed in Table VI, a determination has been made of the effect of reduced temperature on the rate of radiation decomposition of C^{14}-labeled choline chloride. A sample of choline-methyl-C^{14} chloride, containing 10.7 μc/mg, was prepared by reacting methyl-C^{14} iodide with dimethylaminoethanol. The analysis of this compound showed: C, 43.2%; H, 10.3% (theor.); C, 43.0%; H, 10.1% . One-dimensional (BuOH–conc. HCl) and two-dimensional (H_2O–sat. phenol; H_2O–sat. BuOH–propionic acid) chromatograms showed the product to contain less than 1% of radioactive impurities. One portion of this preparation was stored in the dry, crystalline state in the dark in a sealed tube under high vacuum and at room temperature. A second portion was stored under exactly the same conditions except that it was maintained at -196° (liq. N_2) instead of at room temperature. At the end of 46 days, both samples (which by this time had absorbed 1.5×10^6 rep of energy from the C^{14}-betas) were analyzed by means of the paper-chromatographic determination for the amount of trimethylamine hydrochloride formed. The choline chloride stored at room temperature was found to have 27% of trimethylamine present; the corresponding G value is 1,490. No detectable trimethylamine was found on the paper chromatogram of the choline chloride which was stored at -196°. It therefore appears that the decomposition chain reaction for C^{14}-labeled choline chloride is completely inoperative at liquid-nitrogen temperatures.

Table VI

Radiation Decomposition of Choline Analogs

Compound	Type of Radiation	Rep $\times 10^{-6}$	% Decomp.	G (molecules decomp.) (by Reineckate Precip.)	G (trimethylamine formation) (by paper chromatography)
Acetyl choline chloride	1.3-Mev γ	90	6	4	3
Choline chloride	1.3-Mev γ	6.8	28	340	
Choline bromide	1.3-Mev γ	81.0	60	47	
"	"	15.0	19	80	
"	"	6.8	11	102	
Choline iodide	2–4-Mv e^-	230.0	3	0.8	
"	1.3-Mev γ	28.0	3	5.4	1.8
$[(CH_3)_3NCH_2CH_2Cl]^+ Cl^-$	1.3-Mev γ	33.0	0	v. low	
$[(CH_3)_3NCH_2COOH]^+ Cl^-$	1.3-Mev γ	81.0	4	4	2
$[(CH_3)_3NCH_2CH_3]^+ Cl^-$	2–4-Mv e^-	172.0	24	13[a]	
	"	208.0	3	1.3	
"	"	166.0	2	1.1	
	1.3-Mev γ	28.0	1	3.3	
	"	29.0	0	v. low	
	"	52.0	0	"	
	"	29.0	0	"	
	"	50.0	3	5.6	3.7
$[(C_2H_5)_2CH_3NCH_2CH_2OH]^+ Cl^-$	1.3-Mev γ	76.0	24	22	

[a] This value is almost certainly high and is probably due to an error in carrying out the Reineckate analysis.

RADIATION CHEMISTRY OF BENZOIC ACID

Robert M. Noller and B. M. Tolbert

Since the last report on the irradiation chemistry of benzoic acid, two more samples have been irradiated and analyzed. As before, the samples were placed in a break-off tube and sealed after evacuating at about one micron pressure for two hours.

After the irradiation the sample tubes were sealed to a vacuum line and Toepler pump system and opened. The gases and other volatile and sublimable materials were passed through successively colder traps to make a rough separation into convenient fractions. The fractions collected were non-liquid-nitrogen-condensable gases, liquid-nitrogen-condensable gases, and dry-ice-condensable gases. The benzoic acid, which was sublimed out of the irradiation vessel by warming to 120°, was collected in a trap at about -20° C.

The following table lists the gaseous decomposition products that were identified and the G values for their production. Only the totals are shown.

Table VII

Radiation Decomposition of Benzoic Acid

Sample		A	N_2	O_2	H_2	CO	CH_4	CO_2	ØH	H_2O
905.9 mg (1) $ØC^{14}OOH$ received $5.2 \cdot 10^{21}$ ev from Co^{60} γ-source	mMx10^4 per mM ØCOOH			0.11	0.32	0.10	0.02	35.4	3.63	24.8
	G				0.003	0.001	$2 \cdot 10^{-4}$	0.301	0.031	0.211
1071.8 mg (2) $ØC^{14}OOH$ received $4.2 \cdot 10^{21}$ ev from Co^{60} γ-source	mMx10^4 per mM ØCOOH	0.12	1.31	0.25	0.21	0.20	0.002	22.7	1.32	17.4
	G				0.003	0.002	$2 \cdot 10^{-5}$	0.28	0.017	0.219

There has always been a certain small amount of oxygen in the samples. At first this was though to be one of the decomposition products of the benzoic acid. More careful analysis of the mass-spectrographic data, however, revealed that there also were small amounts of nitrogen and argon. The argon would only have come from the air and in the case of sample No. 2 the volume of air calculated on the basis of the argon was 0.028 cc STP and the total volume of oxygen and nitrogen was 0.031 cc STP. The agreement is perhaps fortuitously good in view of the small quantities measured. It is surprising that more of oxygen and nitrogen was not trapped in the crystalline structure.

In the radiation a polymer is formed which does not sublime out of the irradiation vessel even at 140° C. It is yellowish in color and fluoresces with a blue-green color under uv light. In the case of sample No. 1 it was carefully washed out, weighed, and counted. There was a total of 3.23 mg having a specific activity of $3.21 \cdot 10^5$ d/m/mg as against $4.4 \cdot 10^5$ d/m/mg for the benzoic acid. Assuming that the C^{14} content represents polymerized benzoic acid, it may be determined that $26.1 \cdot 10^{-4}$ mM/mM ØCOOH was converted into polymer. From this figure, a G value of 0.22 for polymer formation may be calculated. From the change in specific activity, it appears that benzoic acid or other C^{14}-containing fragments are combining with inactive fragments to form the high-molecular-weight polymer or mixture of polymers.

Attempts have been made to determine the extent of decomposition of the benzoic acid by the isotope dilution method. For such small decompositions, the errors are high and the results not reliable.

Ultraviolet spectroscopy was considered as a means for measuring the extent of decomposition of the benzoic acid. To be most useful, the samples to be irradiated were made small enough so that they could be easily dissolved in the correct amount of solvent for spectrum measurement. Several 15- to 25-mg samples of benzoic acid were carefully weighed and sealed in small evacuated capillaries and irradiated. They were then broken open under the solvent (95% EtOH) and diluted to the correct concentration.

Unfortunately, some of the decomposition products also absorb in the same range as benzoic acid. Until it is known what these substances are, it will be impossible to do more than say that some material was changed.

IRRADIATION OF THIOCTIC ACID AND BISNOR-THIOCTIC ACID

Patricia T. Adams

Samples of 3 to 5 mg of thioctic acid and bisnor-thioctic acid (preparation described in UCRL-2709) were sealed in vacuo in small capillary tubes and subjected to γ-ray irradiation from a 100-curie Co^{60} source. The samples received from $1\text{-}5 \times 10^7$ rep. After irradiation the tubes were opened and analyzed spectrophotometrically for the concentration of unruptured 5-membered disulfide ring. The amount of thioctic acid decomposed was found to be linear with respect to the amount of radiation received. For thioctic acid, $G = \frac{\text{molecules decomposed}}{100 \text{ ev}} = 10$. For bisnor-thioctic acid, G = 18.

The importance of air in measuring reproducible G values was demonstrated. In preliminary experiments, when samples were sealed in air before irradiation, the G value for thioctic acid ranged from 12 to 20, and that for bisnor-thioctic acid varied from 20 to 33.

NUCLEAR CHEMISTRY

Glenn T. Seaborg and Isadore Perlman

STUDIES OF THE PLUTONIUM-239 FISSION PRODUCTS AFTER LONG, INTENSE NEUTRON IRRADIATION

James Robb Grover

About two years ago, 168 milligrams of Pu^{239} was placed in the extremely high neutron flux (3.5 to 3.8 x 10^{14} neutrons/cm^2 second) of the Materials Testing Reactor. In September the products of this irradiation were worked up for the very heaviest elements by Stanley Thompson, Bernard Harvey, and co-workers. A total mass of about 18 mg of plutonium, americium, curium, and elements of higher atomic number were recovered; the recovery was nearly 100%.

The analysis of the remaining 150 mg of material (fission products) and determination of the relative yields were undertaken in this laboratory.

To date, only the yields of the heaviest rare earths have been measured. The procedure was as follows:

1. The rare earths were separated, after some preliminary purification, on a Dowex-50 column with hot lactate elution, employing the feature of continually rising pH as developed by Walter E. Nervik;[1]

2. Each peak was radiochemically assayed, using absolute beta-counting technique, and its decay was followed;

3. Each element was rerun on the column to achieve a substantially higher degree of purification;

4. The lactate was then destroyed, employing hot 30% H_2O_2-concentrated H_2SO_4 mixture, the resulting solution was evaporated, and a suitable aliquot was mounted on a tungsten filament for the mass spectrograph;

5. The isotope distribution for each element was then measured.

Dr. Maynard Michel did the mass spectrograph sample preparation and runs. New glassware was used throughout the chemistry to avoid contamination of the isotopes with natural elements.

The results of the radiochemical assays corrected back to the time of removal from the reactor are as follows:

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[1] W. E. Nervik, private communication.

Nuclide found	Half Life	β-Disintegrations/Minute in Entire Sample	Number of Atoms in Entire Sample
Lu^{177}	6.8 d	$\sim 5 \times 10^{7}$	$\sim 3 \times 10^{11}$
Yb^{175}	4.2 d	6.8×10^{7}	6.0×10^{11}
Tm^{171}	1.9 y	$\sim 1 \times 10^{7}$ [a]	$\sim 1 \times 10^{13}$
Tm^{170}	129 d	8.4×10^{7} [a]	2.2×10^{13}
Er^{169}	9.4 d	1.0×10^{8}	2.0×10^{12}
$Tb^{160, 161}$			
$Y^{90, 91}$			

[a] Al absorption work

As carriers could not be used, the estimation of errors is only approximate, based mostly on following the assay through the second column purification step. The radiochemical yield work is therefore probably no better than ±50% or so.

The relative abundances of isotopes of the various elements were found to be as follows:

Er			Yb		Tm	
Mass No.	Distribution found	Corrected distribution	Mass No.	Distribution found	Mass No.	Distribution found
164	1.35	0.4	168	0.0	169	97
166	52.48	31.5	169	2.0	170	1
167	14.39	0.0	170	5.1	171	2
168	23.25	6.3	171	6.7		
170	9.33	~0.0	172	9.6		
			173	56.4		
			174	2.6		
			175	17.9		
			176	0.0		

For erbium, the amount of natural contamination was estimated by assuming the yield at mass 170 to be zero. This seems approximately correct, because (a) the thermal neutron capture cross section of Er^{168} is ~2 barns, while that for Er^{170} is ~9 barns;[2] and (b) the beta-decay half life of Er^{169} is likely to be short compared with the mean neutron-capture time (this requires

[2] R. F. Barnes, Argonne National Laboratory Report ANL-5287 (July 1954).

that the cross section for thermal-neutron capture be less than a few hundred barns.)

For ytterbium, the appearance of mass number 169 is so far unexplained; mass number 175 comes from known lutetium contamination. The absence of mass numbers 168 and 176 indicates a lack of natural ytterbium contamination.

For thulium, the relative mass yields of 170 and 171 are different by a factor of 4 from those obtained from the attempt at radiochemically separating the two activities by aluminum absorption curve analysis. The extremely high relative abundance of mass number 169 leads one to suspect considerable natural contamination.

In relating the radiochemical yields with the mass distributions, we assumed Y^{175} and Er^{169} to be in a steady state at the time of removal from the reactor, which requires the neutron-capture rate to be small compared to the beta-decay rate. Neutron capture would contribute less than 10% of the rate of disappearance of Y^{175} and Er^{169} if the thermal neutron capture cross sections are: for Yb^{175}, $\sigma_n < 500$ barns; for Er^{169}, $\sigma_n < 250$ barns.

With the known cross sections, neutron flux, and mass of fission products the following approximate yields were calculated, summed for each mass number:

Yield of Pu^{239} Fission Products After Extensive Neutron Capture

Mass No.	Yield %	Apparent Number of Neutrons Captured to Account for the Observed Mass Yield
174	1.7×10^{-5}	5.8
173	3.6×10^{-4}	8.9
172	6.2×10^{-5}	5.5
171	5.5×10^{-5}	4.4
170	3.9×10^{-5}	3.0
169	5.7×10^{-4}	5.5
168	6.4×10^{-4}	4.6
167	~0.0	0
166	3.2×10^{-3}	4.7
	Average	4.7

The "apparent number of neutrons captured" to form the observed mass number was obtained by comparison with the Plutonium Project yield numbers,[3]

[3] K. Way and N. Dismuke, U. S. Atomic Energy Commission Declassified Report AECD-2817 (August 29, 1949).

extrapolated somewhat. The average of 4 to 5 neutrons captured does not seem too unreasonable.

Enough Yb^{175} was recovered to permit a small amount of spectroscopic work on its most abundant gamma rays.

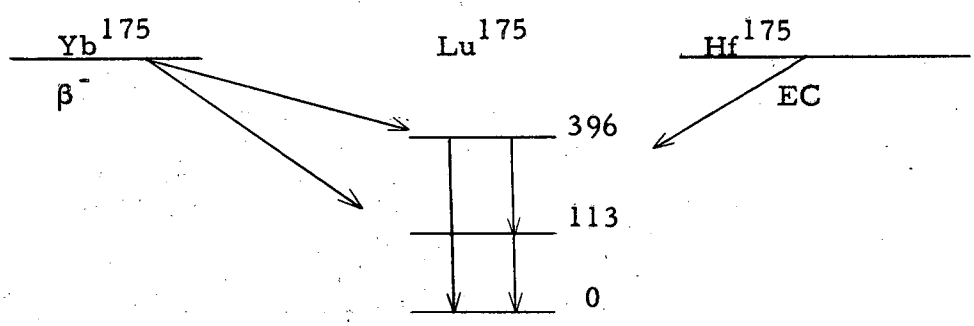
The 50-channel sodium iodide scintillation gamma-ray spectrometer revealed strong K or gamma rays at 55 (lutetium K x-rays), 113, 283, and ~400 kev, and a weak gamma ray at 143 kev. Previously, Cork et al. saw gamma rays at 138, 259, 283, and 396 kev, by the spectroscopy of conversion electrons.[4] These workers did their spectroscopy on several nuclides all mixed together (including Lu^{177}, which has a prominent 112-kev gamma ray), so that they might well have missed the 113-kev gamma ray of Yb^{175}, especially if its conversion coefficients are small.

In cooperation with Frank S. Stephens, the following coincidences were established:

1. (113) (K x-rays, 283)
2. (283) (K x-rays, 113)
3. (400) (nothing)

Here, for each coincidence experiment, the first set of parentheses indicates the energy in kev of the gamma ray used as the gate, and the second set encloses the energy in kev of the gamma rays found in coincidence.

A probable partial decay scheme is as follows:



The 283-kev transition is placed above the 113-kev transition because a 113-kev gamma ray is also found with the gamma rays from the EC decay of Hf^{175}, among which no corresponding 283-kev gamma ray has been observed.[5]

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[4] J. M. Cork, H. B. Keller, W. C. Rutledge, and A. E. Stoddard, Phys. Rev. 78, 95 (1950).

[5] J. M. Hollander, I. Perlman, G. T. Seaborg, Revs. Modern Phys. 25, 469 (1952).

NEUTRON-DEFICIENT ISOTOPES IN THE HAFNIUM-LUTETIUM REGION

John T. Worthington

Further work has been done in the investigation of the neutron-deficient isotopes in the hafnium-lutetium region. Cyclotron bombardments, using 100-Mev protons, were made on $Hf(NO_3)_4$, and the resulting hafnium activities were separated in the usual manner. Previously, milkings of the hafnium were made by precipitation of the daughter lutetium as fluoride with lanthanum as a carrier. This was found to be unsatisfactory, as the milkings did not follow a definite trend in their activity, and it was thought that some hafnium was carried along in the precipitation. A new milking technique was developed whereby the hafnium was taken up in 0.5 M TTA dissolved in benzene. The daughter lutetium was obtained by successive back-extractions of this solution with 0.1 M HCl. These milkings were found to be quite clean.

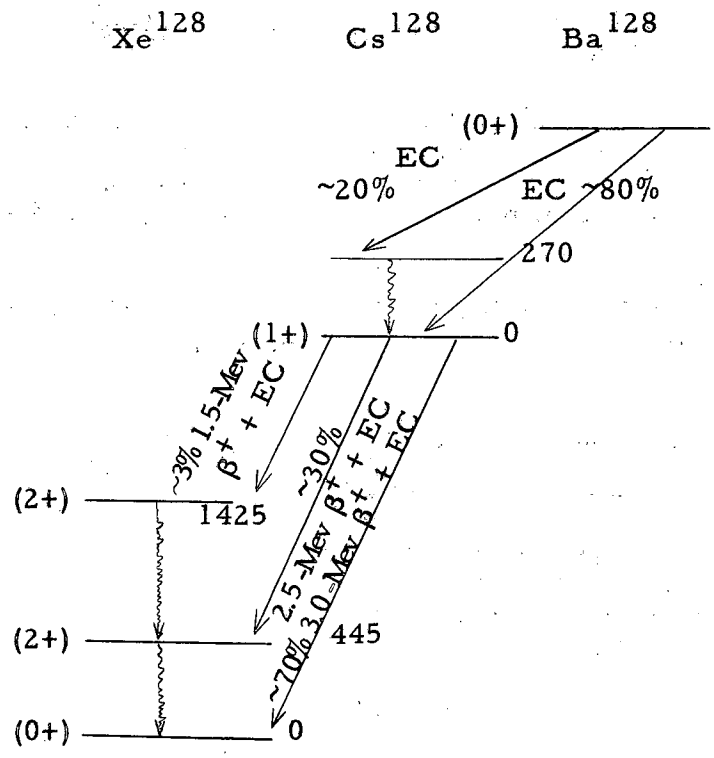
In the lutetium fractions, half lives of 1.7 days and 8.5 days were observed--probably corresponding to Lu^{170} and Lu^{171}, respectively. In the parent fraction, besides these half lives, there occurred a 17- and a 1.7-hour activity presumably due to Hf^{171} and Hf^{170}, respectively. A long-lived component >40 days was also present in both fractions. The 1.7-hour half life was observed as a 0.510 (positron) peak on the 50-channel gamma analyzer. A gamma ray of 290 kev with a half life of 17 hours was also observed.

Further work on the parent-daughter relationship is now in progress.

RADIATIONS OF BARIUM-128-CESIUM-128

Jack M. Hollander and Marvin I. Kalkstein

The chain Ba^{128}-Cs^{128} has been prepared in the 184-inch cyclotron by the reaction $Cs^{133}(p,6n)Ba^{128}$, and its radiations have been studied with a 50-channel scintillation spectrometer, a scintillation coincidence spectrometer, and a magnetic-lens spectrometer. Gamma rays of energy 445 kev and 980 kev belonging to the decay of Cs^{128}, have been observed. A 270-kev gamma ray is observed in the decay of Ba^{128}. The beta-ray spectrometer data indicate three positron groups of end-point energies 3.0, 2.5, and 1.5 Mev with relative abundances of 7:3:0.3, respectively. These belong to the decay of Cs^{128}, which decays mainly by positron emission with a ratio of β^+/EC of 3:1. The decay of Ba^{128} is entirely by electron capture. The conversion coefficient for the 445-kev gamma ray is 0.016. The 270-kev gamma ray has a conversion coefficient of 0.35 and a K:L ratio of ~2.5. The results of the coincidence experiments, both for gamma-gamma coincidence measurements and for beta-gamma coincidence measurements, are consistent with the above facts. The following decay scheme is proposed.



FAST-COINCIDENCE WORK ON CALIFORNIUM

Donald Strominger, Charles R. Gallagher, Jr., and John O. Rasmussen

A mixture of Cf^{249}, Cf^{250}, and Cf^{252} has been investigated with the fast-coincidence apparatus previously reported by Rasmussen and Kalkstein.[1] By alpha activity the sample contained 33% Cf^{249} and 67% Cf^{250} and Cf^{252} combined.

A stilbene scintillation counter was used to detect alpha particles and a sodium iodide (thallium iodide activated) crystal was used to detect gamma transitions in coincidence with the alpha particles. The 50-channel pulse-height analyzer was used to study the coincident gamma spectrum. A single-channel pulse-height discriminator was used for the alpha-counter pulses.

In coincidence with the alpha particles were found electromagnetic radiation peaks of ~25 kev, 340 kev, and 395 kev. In addition, there was a broad peak from about 60 to 120 kev.

The gamma-ray spectrum in coincidence with alpha particles was examined at various delay times. In this way an upper limit of 1.9×10^{-9} second can be set for the half life of the level from which the 394-kev (and presumably the 340-kev) radiation emanates.

[1] J. O. Rasmussen and M. I. Kalkstein, Chemistry Division, Quarterly Report, University of California Radiation Laboratory Report No. UCRL-2531.

Both the 25-kev peak and the broad peak of about 100 kev decay with a half life of about 3.3×10^{-8} second. The 25-kev radiation could be L x-radiation resulting from internal conversion of gamma transitions involved in the decay of the isomeric state.

It is presumed that the delayed coincidences are associated with the decay of Cf^{249}, the odd-mass alpha emitter, rather than from the even-even nuclides, Cf^{250} or Cf^{252}, as isomers in this half-life range have never been observed for even-even nuclei but are not uncommon for odd-mass nuclei in the heavy region.

We are grateful to Dr. Stanley G. Thompson and others of the heavy-element research team for the preparation and loan of this californium sample.

ALPHA DECAY OF SPHEROIDAL NUCLEI

John O. Rasmussen and Ben Segall[1]

Several numerical integrations of the coupled wave equations[2] for Cm^{242} alpha decay have been carried out in prolate spheroidal coordinates. The following nuclear boundary conditions at the spheroidal surface have been tried:

I and II $\psi_{surface}$ assumed constant over nuclear surface. (Two choices of nuclear radius.)

III and IV $\psi_{surface}$ given by one-body model of alpha in its lowest energy state in a spheroidal potential well. (Two choices of nuclear radius.)

The resulting relative intensities for the $\ell = 0$, $\ell = 2$, and $\ell = 4$ alpha groups are in the above cases about right for the 2:0 ratio, but are in all cases considerably larger than experimental 4:0 ratios.

The procedure was reversed, and the experimental intensities were used to set the boundary conditions at large distance (though relative signs must be assumed), and the integration was carried in to the nuclear surface. The resulting wave function shows the greatest probability of emission from that part of the nuclear surface halfway between the poles and the equator.

The fundamental conclusion to be drawn is that "alpha clusters" of proton and neutron pairs have only a transitory existence in nuclear matter. If these clusters, once formed, traversed the nuclear dimensions many times before dissolving, the one-body model should have given better agreement. The best picture of alpha decay now must be that alpha clusters are continually forming and dissolving in nuclear matter, those formed in the surface region with high kinetic energy having a chance at penetrating the barrier. Thus the

[1] Now with Solid State Physics Research Group, General Electric Company, Schenectady, New York.

[2] See J. O. Rasmussen, University of California Radiation Laboratory Report No. UCRL-2431, and previous Chemistry Division Quarterly reports.

most probable parts of the nuclear surface for alpha emission are those parts where there is a maximum overlap of the wave functions of the most lightly bound proton and neutron pairs. The order of level-filling in a prolate spheroidal nuclear well first involves wave functions large near the poles and then progresses through those large at intermediate angles to those large at the equator. Cm^{242} is evidently near the middle of a shell-filling, as evidenced by the near constancy of rotational moments of inertia. Its most lightly bound nucleons probably have wave functions large at intermediate angles between poles and equator, consistent with the alpha-decay results above.

Numerical calculations for Th^{228} alpha decay are in progress.

NUCLEAR QUADRUPOLE RESONANCE

Gilbert O. Brink, Alan H. Reddoch, and Burris B. Cunningham

An antisymmetric square-wave generator has been built and tested and found to work satisfactorily. Owing to the lack of 110 volts dc, it was necessary to design the equipment to work from 6-volt storage batteries. Western Electric WE-275-C mercury relays were used instead of the conventional 6AS7's to switch the current for the modulation coils. The modulation frequency used is 50 cps with the signal appearing at 100 cps. With this arrangement the amplitude pickup should be reduced by a factor of about 1000.

Work is in progress to attempt to increase the sensitivity of the equipment in order to allow smaller samples to be used. If small enough samples can be used, a search for the O^{17} resonance in Lu_2O_3 will be conducted. In any case, it is planned to look for the Lu^{175} resonance in this compound.

MASS SPECTROSCOPY

Fred L. Reynolds and Russell G. Herron

The possible use of a point field-emission ion source in mass spectroscopy, particularly for very small solid samples, has interested us for a period of time. Müller[1] first described the field-emission microscope in 1936. The construction of such a microscope is shown in Fig. 1.

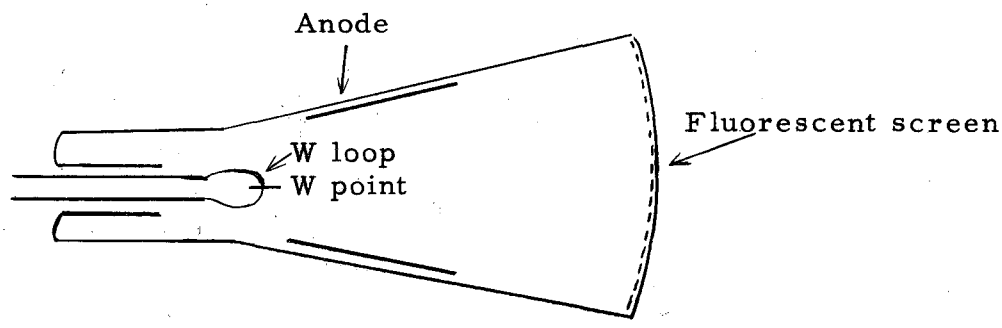


Fig. 1

[1] E. W. Müller, Physik. Z. 37, 838 (1936).

Müller applied to the anode a positive potential of about 10 kv, giving fields of about 50 million volts per cm^2 at or near the surface of the point. His points had a radius of curvature at the tip of about 1×10^{-4} to 1×10^{-5} cm. The magnification of the field-emission microscope is a function of the point-to-screen distance divided by the point radius. It is commonplace to obtain magnifications of 10^6 and a resolution of about 20×10^{-8} cm. Under these conditions sufficient electrons are pulled from the point at room temperatures to produce a visible surface picture of the point on the fluorescent screen.

Our interest is in producing positive ions using the point field-emission technique, by reversing the field polarity and impinging the sample on the point by various suitable methods. Most of the field microscope literature is concerned with electron emission, but Müller[2] did try positive-ion emission, using hydrogen as the sample gas. He found that it was possible to pull off protons from the point with fields at the point near 200 million volts per cm^2.

As a preliminary experiment, it was decided not to construct a fluorescent-screen type of tube, but to use a metal anode and detect the signal with a dc electrometer. The tube construction is shown in Fig. 2.

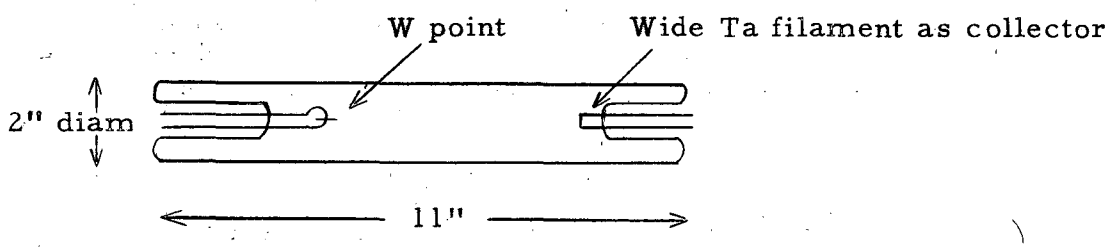


Fig. 2

Mostly in order to gain experience in the techniques involved in this type of experimentation, we chose to try to repeat the hydrogen-proton experiment using the tube previously described. A block diagram of the system is as follows:

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[2] E. W. Muller, Physik. Z. 131, 136 (1951).

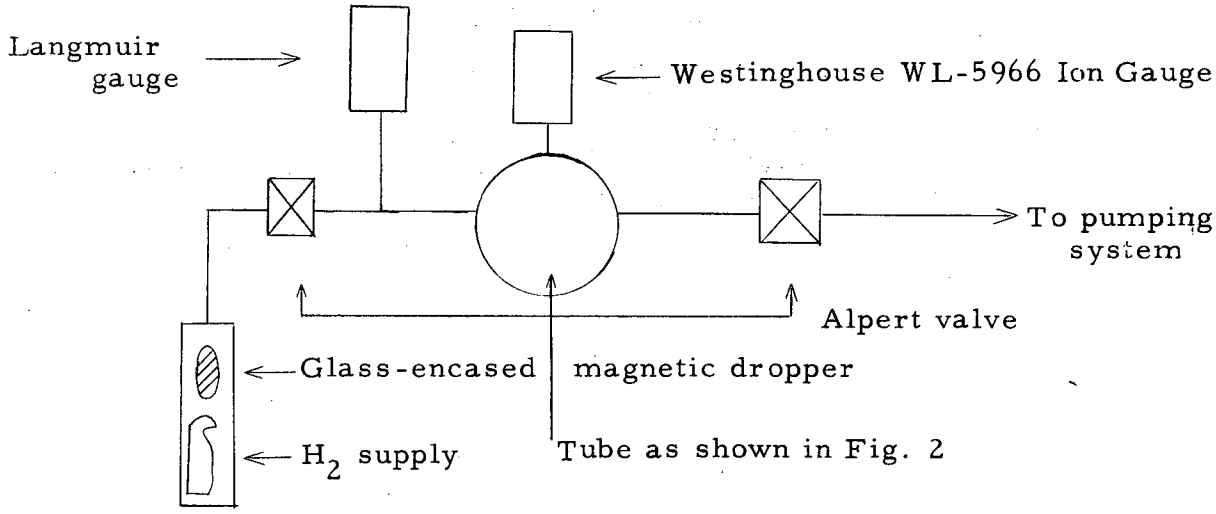

Fig. 3

The high-vacuum technique follows closely that of Alpert[3]. The system as shown is baked at 425°C until the pressure is about 10^{-7} mm Hg. The metal parts are outgassed by passing current through the filaments, and the ion gauge is outgassed by electron bombardment. The valve on the right is then closed and the WL-5966 acts as an ion pump, reducing the pressure within several hours to 10^{-9} mm Hg. Next, the left valve is closed and the hydrogen break-off is broken. Hydrogen is then introduced into the main tube by cracking the left valve, and pressures of hydrogen between 10^{-2} and 10^{-4} are read off the Langmuir[4] gauge.

Before the introduction of hydrogen the point is flashed at 2500°C until there is no detectable current on the electrometer when the anode is at 40 kv and the point is at room temperature. The hydrogen is then introduced. The following preliminary qualitative results have been obtained with the point at room temperature.

With a hydrogen pressure of 2×10^{-2} mm Hg and an anode voltage of 40 kv we obtained a current reading of 4×10^{-11} ampere. When the gas was slowly pumped out the current followed the reduction in gas pressure, and the electrometer reduced to zero when a vacuum of 10^{-7} had been reached. From kinetic theory, the number of molecules of hydrogen at 2×10^{-2} mm Hg hitting a half sphere of radius 10^{-4} cm is 9×10^{11} per sec. From the current collected and the geometry of the tube we calculated that between 13% and 16% of those hitting are ionized as protons. With certain changes in tube design we will be able to get more quantitative data. We plan to associate this equipment with a mass spectrometer, as described by Inghram and Gomer[5] in a recent letter to the editor of the Journal of Chemical Physics.

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[3] D. Alpert, Scientific Paper No. 1695, Westinghouse Research Laboratory.
[4] I. Langmuir, J. Am. Chem. Soc. 35, 107 (1913).
[5] Inghram and Gomer, J. Chem. Phys. 22, 1279 (1954).

DOUBLE-RETARDING-FIELD ELECTROSTATIC BETA-RAY SPECTROMETER

Herbert R. Johnston

The original design for this instrument included a 12-stage secondary electron multiplier. The first two dynodes were made in the laboratory sheet metal shop and the last ten were obtained as a unit from the Du Mont Laboratories. This last group of dynodes was the secondary electron multiplier designed by Du Mont for use in their 2-inch-diameter photomultiplier tube.

The design also included a coil of copper tubing placed around the secondary electron multiplier. This coil was to serve the double purpose of heating the dynodes by induction with radiofrequency current and cooling them by radiation when the copper coil was filled with liquid nitrogen. The radiofrequency induction heating was part of a scheme to activate the dynodes after installation in the device, and also after any subsequent exposure to air.

When attempts were made to heat the dynodes of the secondary multiplier, it was found impossible to raise them all to a uniform temperature. Some dynodes got too hot before others reached even one-half of the required temperature (approximately 550°C.) for activation. Consequently it was impossible to obtain sufficient sensitivity out of the multiplier to properly operate the beta-ray spectrometer.

It was decided to replace the multiplier installed in the device by another of a different design. This new secondary electron multiplier is essentially identical to multipliers built by Fred L. Reynolds and used in the mass spectrometers. The silver-magnesium dynodes are processed before assembly by a method involving the use of heat and water vapor when the dynodes are under vacuum. The method is essentially the same as that described by P. Rapport in the Journal of Applied Physics, March 1954.

In the new design, no provision is being made to heat or cool the dynodes of the multiplier. The dynodes are activated before assembly, and experience has shown that this type of multiplier may be exposed to air for many hours without losing more than a small percentage of its gain. Also, it has been found that the thermal or dark current for the silver-magnesium metal is very low, since the work function is large. This fact will make it unnecessary to cool the multiplier during operation.

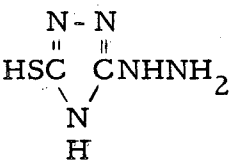
The new multiplier will have a total of 18 stages and will probably have gains of the order of 10^7. With this kind of gain, it will be possible to dispense with the present preamplifier and feed the output directly in to the scaler.

Work on the installation of the new secondary electron multiplier is under way at the present time.

SPACE GROUPS

Michael E. Senko and David H. Templeton

The space group of $CH_3\overset{S}{\overset{|}{C}}NHNH\overset{S}{\overset{|}{C}}NH_2$ has been determined to be Cmca, with a = 11.39 Å, b = 27.68 Å, and c = 9.65 Å, 16 molecules per unit cell. No further work on this compound is contemplated at the present time.

The space gruop of 

was found to be $P_{2_1/c}$ with the following lattice parameters: a = 4.74 Å, b = 15.58 Å, c = 7.32 Å, β = 108°35', with 4 molecules per unit cell. At present intensity photographs are being taken in preparation for a Harker-Patterson section, which will be the next step in a possible determination of this structure.

The space group of the compound KF·2HF has been found to be $P_{2_12_12_1}$, a ~6.70 Å, b ~11.0 Å, and c ~8.5 Å, 8 molecules per unit cell. Work is continuing on other compounds of the system KF·xHF.

STRUCTURE OF INDIUM IODIDE

Robert E. Jones, Jr., and David H. Templeton

Work toward the determination of the structure of InI has been commenced. From Weissenberg pictures of a single crystal of this substance the following features were determined: (a) InI is orthorhombic with unit cell dimensions 4.77, 12.73, and 4.83 Å, respectively; (b) its space group is D_{2h}^{17}(Cmcm); (c) the structure seems to be very close to that of the low-temperature form of TlI, very likely differing only in the values of the two parameters describing the two structures.

A satisfactory method for making InI_3 has been found. It is produced by sealing In and I_2 in an evacuated tube and heating the In to 300° C. If the tube is allowed to remain at these conditions for three days or more, satisfactory single crystals can be grown. The next step in the structural determination of InI_3 will be use of these single crystals in the oscillation and Weissenberg cameras.

CHEMICAL ENGINEERING (PROCESS CHEMISTRY)

NOTES ON WORK IN PROGRESS

Capacity of Perforated-Plate Liquid-Vapor Contacting Columns

Charles d'A. Hunt, Donald N. Hanson, and Charles R. Wilke

This work has been completed and the results have been published in UCRL-2696.

Stability of Perforated Plate Trays

Robert S. Brown, Donald N. Hanson, and Charles R. Wilke

Work has been started to extend the correlations on capacity of perforated trays developed by C. D. Hunt. Equipment is being designed to determine the factors that influence tray stability with respect to liquid dumping. The equipment consists of a positive-displacement blower capable of circulating 4,000 cfm at 1 psig, a rectangular column with a single plate 1.5 by 2 ft, and a pump with a rated output of 500 gpm. It is planned to circulate gases ranging from helium to freon through the plate while flowing liquid over the plate and measuring the amount of dumping of liquid through the tray.

Gas-Phase Mass Transfer Studies

Loren J. Hov and Charles R. Wilke

Psychrometric studies are being continued and new sampling systems are being installed. Vapor pressure of naphthalene cylinders has been determined using air as inert gas, and determinations using Freon 12 and helium are in progress.

Vacuum Flow through Annular Sections

Walter Dong, Donald N. Hanson

Experimental work on vacuum flow between parallel copper plates is completed. Theoretical analysis of the results is in progress.

Thermal Conductivity of Gases at High Temperatures

Henry Cheung and Charles R. Wilke

Plans have been made for the installation of an overhead rail-and-pulley system to facilitate fitting of the 900-lb copper block-thermal conductivity cell assembly into the furnace. Engineering drawings have been completed and action has been taken the secure the necessary parts.

A flow system composed of capillary flow meters for mixing gases to be introduced into the thermal conductivity cell has been installed.

GENERAL CHEMISTRY

W. M. Latimer, Director

METALS AND HIGH-TEMPERATURE THERMODYNAMICS

Leo Brewer, Richard Brewer, John Engelke, William Hicks, James Kane, Oscar Krikorian, Geoffrey James, Lewis Roberts

Determination of Ground States of Gaseous C_2 and SO

Some evidence for the SO bands in absorption have been found but they have not yet been confirmed using the 21-foot grating. A cesium oxide detector is now in operation for study of the infrared bands of C_2, but the bands have not been observed to date.

Gaseous Carbon Species

The heat of sublimation of $C_2(^3\pi)$ has been determined to be 200 kcal by comparison of the temperature coefficient of the Swan bands with Zr atomic lines. The results are being checked by a similar comparison with Ti atomic lines.

Study of Molybdenum Gaseous Halides and Oxy-Halides

Evidence has been obtained that indicates that MoO_2OHCl is the gaseous molecule interfering with the molybdenum chloride studies. Work is under way to establish the formula more definitely and to obtain the thermodynamic properties of the molecule.

Vaporization and Condensation Coefficients of Molecular Beams

A paper has been submitted to the Journal of Physical Chemistry summarizing the results to date. Further work is under way to extend the measurements taken with arsenic and phosphorus and to try additional vaporization catalysts. Mass-spectrometer measurements will be necessary to completely elucidate the systems.

Refractories

A paper has been submitted to the Journal of the American Electrochemical Society summarizing our work with metal boride ternary diagrams and listing the resulting thermodynamic data. A paper covering our work with silicides is virtually complete. Examination of bond energies of these refractory compounds has shown many interesting variations that yield a good deal of insight into the nature of the bonding in the high-melting refractory compounds.

Oxide Reaction Studies

The study of exchange of oxygen in UO_2-ThO_2 solid solutions is just starting up. It is hoped that these measurements will shed light on the mechanism of oxidation of uranium in oxide systems.

BASIC CHEMISTRY, INCLUDING METAL CHELATES

John Below, Howard Cady, Robert E. Connick, Laddie Griffith, Armine Paul and Robert Wood

The Entropy of the Selenide Ion in Aqueous Solutions

The second ionization constant of H_2Se in 1 M KOH solutions is being measured. The pK_A is about 14.

Chemistry of Ruthenium

During the past quarter, work on the preparation of uncomplexed Ru_{III} has been performed. Preliminary results indicate that oxidation of Ru_{III} with RuO_4 or Ce^{+4} yields a product in oxidation state 4.3.

The Spectrophotometric Study of Rapid Reactions

The rapid mixing and spectrophotometric recording equipment previously described has been used to study the reaction between ceric perchlorate and ferrous perchlorate. A bimolecular rate constant at 22 ± 1°C and 1 M perchloric acid of $4.0 \pm 0.5 \times 10^3\ M^{-1} - sec^{-1}$ has been found. This may be compared with a value of $5.0 \times 10^3\ M - sec^{-1}$ interpolated from unpublished data of Autrey and Connick. The difference is not yet resolved.

Oxidation of the stainless steel mixer by the acidic ceric solutions has occurred, and a protective coating has been devised and tested.

Further Results of Fluoride Complexing Experiments

The fluoride complexing of Cu^{++}, Zn^{++}, Ag^{+}, and Hg^{++} is being studied at 15° and 35°C to obtain the heats and entropies for the complexing reactions. For Cu^{++}, Ag^{+}, and Hg^{++}, the temperature coefficients are quite small. The Zn^{++} calculations are not yet complete.

Since the complexing is so weak for all of the above ions, and since less than one per cent of the total metal present is complexed in the case of Cu^{++} and Zn^{++}, the complexing of these two ions is being restudied using different sources of $Cu(ClO_4)_2$ and $Zn(ClO_4)_2$ to check on the presence of impurities.

The fluoride complexing of Hg^{++} was restudied using a slightly different technique in which the acidity was kept constant. Although the effect was smaller, the results agreed reasonably well with those obtained using the original technique.

Considerable work was done on the fluoride complexing of Sn^{++}. Most of the experiments were performed using a concentration cell containing Sn amalgam-Sn^{++} electrodes. At Sn^{++} concentrations greater than about 0.01 M, and at acidities less than about 0.5 M, the results are uninterpretable on the basis of a simple complexing reaction. Under the conditons of 0.01 M > Sn^{++} > 0.003 M and 1.7 M > H^{+} 0.5 M, the results can be fairly well interpreted assuming the principal species is SnF^{+}. The data do not fit such a picture as well as they should, and become progressively worse as the Sn^{++} concentration is raised and the acidity lowered. The stability of the SnF^{+} complex is of about the same order of magnitude as reported in the recent paper of Scaap.

Further work must be done before the problem is solved.

Radiation Induced Reactions in Non-aqueous Solutions

Investigation is being carried on of the rate of disappearance of diphenyl-picryl-hydrazyl in chloroform, benzene, toluene and carbon tetrachloride in the presence of radiation of 2537 Å wave length, as well as the absorption spectra of the products formed. Preliminary experiments have been done both in the presence and absence of air and the results show that the reaction in both cases is of a complicated nature. A more intensive study of the kinetics of the reaction is now being done.