DECLASSIFIED

DECLASSIFIED

UCRL 127
cy 67/A
C2

SECRET

UNIVERSITY OF CALIFORNIA

Radiation Laboratory

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

BERKELEY, CALIFORNIA

UCRL-127
C.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UNIVERSITY OF CALIFORNIA
RADIATION LABORATORY

Cover Sheet
Do not remove

INDEX NO. UCRL-127
This document contains 17 pages
and — plates of figures.
This is copy 67 of 80. Series A

Issued to: INFO DIV.

DECLASSIFIED

~~SECRET~~
Classification

Each person who received this document must sign the cover sheet in the space below.

Route to	Noted by	Date	Route to	Noted by	Date
CHEMISTRY DIVISION					
G. T. Seaborg					

DECLASSIFIED

UCRL-127

SECRET

Special Review of Declassified Reports
Authorized by USDOE JK Bratton
Unclassified TWX P182206Z May 79

REPORT PROPERLY DECLASSIFIED

J. N. Green 8-16-79
Authorized Derivative Classifier Date

Linda Cohen 8-20-79
By Date

UNIVERSITY OF CALIFORNIA

Radiation Laboratory

Contract No. W-7405-Eng.-48

CLASSIFICATION CANCELLED
BY AUTHORITY OF THE DECLASSIFICATION BRANCH USAEC per TID 1113
BY B Forbett 3-31-56
SIGNATURE OF THE PERSON MAKING THE CHANGE DATE

CHEMISTRY DIVISIONS

QUARTERLY REPORT MARCH 1948 to MAY 1948

CAUTION

This document contains information affecting the National Defense of the United States. Its transmission or the disclosure of its contents in any manner to an unauthorized person is prohibited and may result in severe criminal penalties under applicable Federal laws.

July 23, 1948

Berkeley, California

DECLASSIFIED

SECRET

Standard Distribution	Copy Nos.
Argonne National Laboratory	1-10
Atomic Energy Commission, Washington	11-12
Brookhaven National Laboratory	13-20
General Electric Company	21-24
Hanford Directed Operations	25-31
Iowa State College	32
Kellex Corporation	33-34
Los Alamos	35-37
Naval Radiological Defense Laboratory	38
NEPA	39
New York Directed Operations	40-41
Oak Ridge National Laboratory	42-49
Patent Advisor, Washington	50
Technical Information Division, ORDO	51-65
University of California Radiation Laboratory	66-70
University of Rochester	71-72
Office of Chicago Directed Operations	73
University of California	
I. Perlman	74
B. Tolbert	75
W. Latimer	76
E. Segre	77
J.G. Hamilton	78
E.O. Lawrence	79
Patent Dept.	80
Total	80

Information Division
Radiation Laboratory
University of California
Berkeley, California

DECLASSIFIED

SECRET

TABLE OF CONTENTS

I. Quarterly Report. Project 48. Page

A. Chemistry of the Actinide and Lanthanide Elements. . . 4

B. Chemistry of Astatine. 5

C. Bio-Organic Chemistry. 7

II. Quarterly Report. Project 48B.

A. Metals and High Temperature Thermodynamics. 15

B. Basic Chemistry, Including Metal Chelates. 15

 DECLASSIFIED

SECRET

I. Quarterly Progress Report. Project 48

A. Chemistry of the Actinide and Lanthanide Elements and Nuclear Transformations

I. Perlman

This subject will be fully reported in the next Quarterly Report.

DECLASSIFIED

B. Chemistry of Astatine.

G. L. Johnson, R. F. Leininger, E. Segre

Electrochemistry.

Oxidation by bromine will prevent completely the reduction of astatine at the cathode under conditions where reduction had previously been observed. See the Quarterly Chemistry Report, December 1947 to February 1948 (UCRL-71). In addition, if astatine is deposited on the gold cathode and bromine is then added to the solution, the astatine is very rapidly removed from the gold. Bromine oxidation has no effect upon the deposition of astatine upon a gold anode. The critical deposition potential observed was -1.44 ± 0.02 volts.

Attempts to date to observe the depositions of astatine at the cathode in solution of different pH have been unsuccessful. One very crude result indicated that the deposition reaction involves two hydrogen ions per astatine ion deposited.

A possible reaction is:

$$At\,O^- + e^- + 2H^+ \longrightarrow At^0 + H_2O$$

Additional measurements must be made to confirm this result.

Volatility Experiments.

HBr and HI solutions containing astatine have been distilled and the distillate collected in small fractions and separately counted. With either acid, less than 1 percent total of the astatine was found in the distillate. There was a tendency for the astatine to come over as the activity became concentrated in the distillation pot. Good material balances were found with both distillations.

Carrying Experiments.

Sulfides. In the last quarterly report and in the paper by Segrè[1], carrying of astatine by silver, mercuric, and bismuth sulfides was reported. Since these elements form insoluble iodides, the possibility that the astatine was being reduced by sulfide and the corresponding astatides were being carried down was considered. The experiment was repeated with cadmium sulfide as the carrier since cadmium iodide is very soluble. As a function of acidity the sulfide carried as follows:

Acidity (HCl)	Percent Astatine Carried
0.025M	88
0.1	82
0.3	86

In view of this result no good theory as to the mechanism of the sulfide carrying exists at the time of writing.

Iodides. Since solvent extraction studies have shown that astatine is incompletely reduced by SO_2, the complete carrying by silver iodide is anomalous. When the experiments are repeated using thallous iodide, poor carrying is observed. The carrying by silver

1. Corson, Mac Kenzie and Segrè, Phys. Rev. 58, 672 (1940).

iodide is probably due to the reduction of silver and the adsorption of the astatine on the metallic surface. The strong absorption of astatine by silver has been noted in a previous report. An experiment to be described demonstrates the point.

When a 0.1 molar solution of astatine was treated with the compounds listed below and the mixture centrifuged, the percent of astatine precipitated in each case was as follows:

Experiment No.	1	2	3	4
Treatment	Saturated SO_2	.001M Ag^+	Saturated SO_2	0.001M Ag^+
Percent of Astatine Precipitated	12	16	7	21

However when the following compounds were added to the above solutions the percent precipitated was as follows:

Solution	1	2	3	4
Quantity Added	0.001M Ag^+	Saturated SO_2	0.0001M Ag^+	Saturated SO_2
Percent of Astatine Precipitated	78	87	86	96

This illustrates rather strikingly the effect predicted.

Thallous and Silver Iodide after Zn Reduction. When the astatine is previously reduced in the presence of iodide by Zn - either plain or amalgamated - and either silver or thallous nitrate added to the reduced astatine solution, the astatine is carried completely.

The net result of these experiments is that SO_2 is not a strong enough reducing agent and zinc is more than ample, which would place the potential for the minus one - astatine - couple at about +0.10 volts with respect to a normal H_2 electrode.

Very little activity remains on the plain zinc after reduction ($<$ 5%). More activity ($<$ 20%) is adsorbed by the amalgamated zinc.

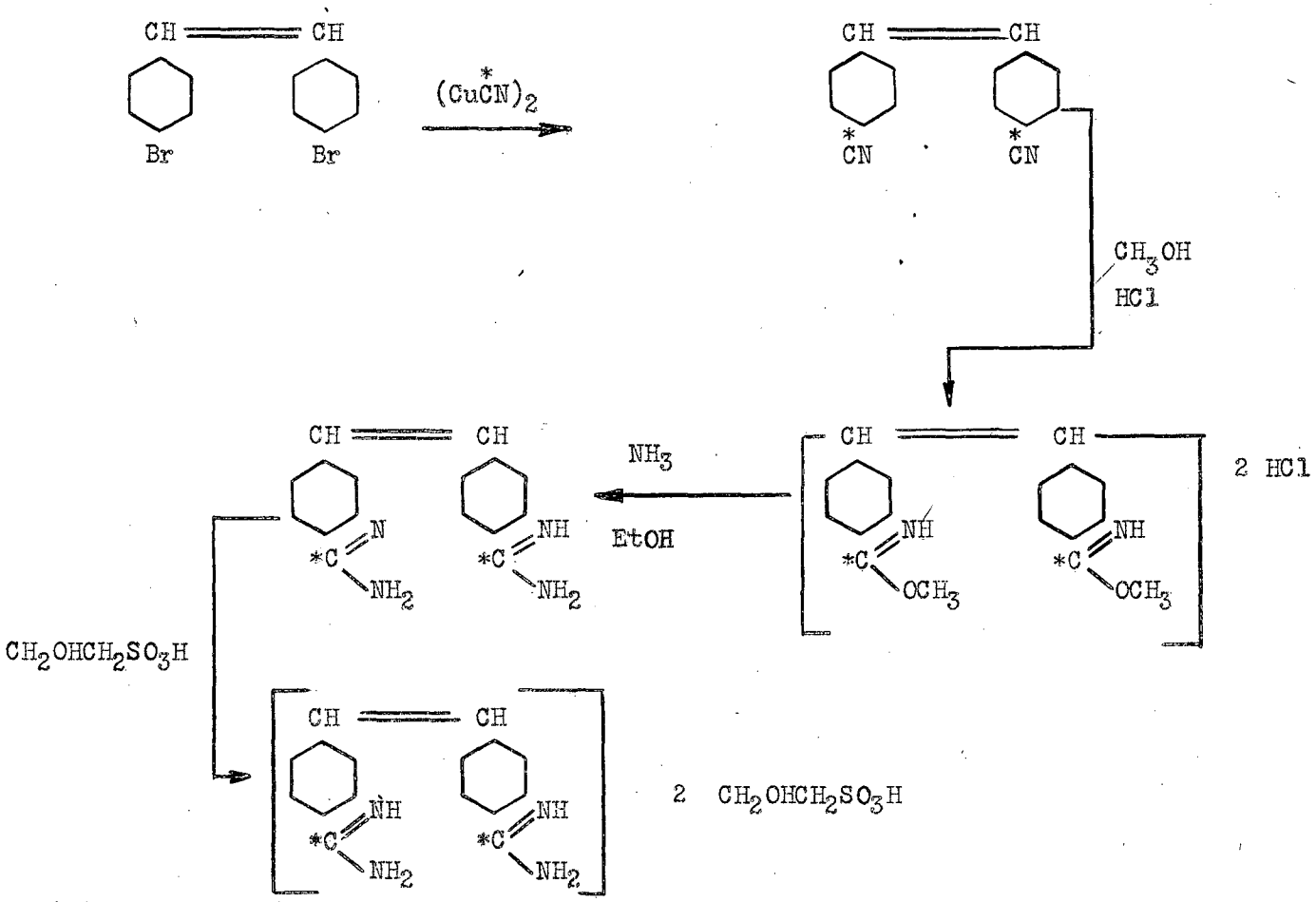
C. Bio-Organic Chemistry.

B. M. Tolbert

Synthetic and Experimental Organic Chemistry.

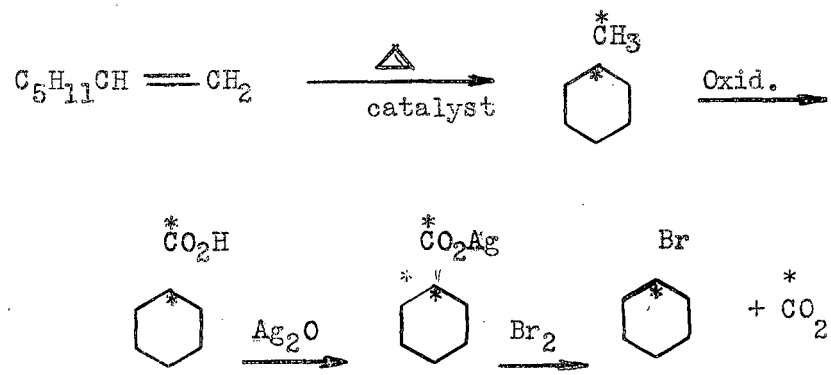
Synthetic Chemistry. The synthesis of a number of C^{14} labeled compounds is being studied. In the following section, the preparation schemes are outlined and proposed uses of the labeled material are briefly stated.

Stilbamidine, 4,4'-stilbenedicarboxamidine diisethionate.



This compound is being synthesized to investigate its behavior in multiple myeloma in which, according to previous reports in the literature, it has chemo-therapeutic effect associated with a tendency to localize in the neoplastic tissue. Inactive preparations of this compound on a small scale have been carried out, and a low activity run is now in progress preparatory to a high specific activity run.

Bromobenzene-1-C^{14}, C_6H_5Br. The preparation of heptene-1-C^{14} has been described in the last Quarterly Progress Report. In connection with the University of California Chemistry Department this compound has been converted to toluene by cyclic dehydrogenation, and the toluene then degraded to bromobenzene as follows:



Preliminary experiments indicate that the activity in the 1-position of the heptene is found both in the ring and in the methyl group of the toluene. Experiments are being continued on the effect of variation in catalyst contact time on the position of label of both the toluene and the unreacted heptene-1. In the experiments conducted thus far, about one-third of the activity found in the toluene is in the methyl group and about two-thirds in the ring, indicating that ring-closure can occur by several different paths. Variations in the condition of the cyclization may very well change this activity ratio appreciably.

<u>Choline Chloride and Acetylcholine Chloride</u>, $[(\overset{*}{C}H_3)_3NCH_2CH_2OH]Cl$ and $[(\overset{*}{C}H_3)_3NCH_2CH_2OCOCH_3]Cl$.

$$\overset{*}{C}O_2 \xrightarrow{H_2} \overset{*}{C}H_3OH \xrightarrow{P_4I_2} \overset{*}{C}H_3I \qquad \underline{(\overset{*}{C}H_3)_2NCH_2CH_2OH}$$

$$[(\overset{*}{C}H_3)_3NCH_2CH_2OH]\,I \xrightarrow{Ag_2O} [(\overset{*}{C}H_3)_3NCH_2CH_2OH]\,OH \xrightarrow{HCl}$$

$$[(\overset{*}{C}H_3)_3NCH_2CH_2OH]\,Cl \xrightarrow{CH_3COCl} [(\overset{*}{C}H_3)_3NCH_2CH_2OCOCH_3]\,Cl$$

Choline Chloride — Acetylcholine Chloride

Low activity runs have been carried out and high specific activity material will shortly be prepared. These compounds will be used in metabolic studies.

<u>Alanine-1-C^{14}</u>, $CH_3CHNH_2\overset{*}{C}O_2H$.

$$CH_3CH_2\overset{*}{C}O_2H \xrightarrow[P]{Br} CH_3CHBr\overset{*}{C}O_2H \xrightarrow{NH_3} CH_3CHNH_2\overset{*}{C}O_2H$$

<u>Alanine-2-C^{14}</u>, $CH_3CHNH_2\overset{*}{C}O_2H$

$$CH_3\overset{*}{C}O_2H \xrightarrow[(C_2H_5)_2SO_4]{} CH_3\overset{*}{C}O_2C_2H_5 \xrightarrow{H_2} CH_3\overset{*}{C}H_2OH \xrightarrow{P,I_2}$$

$$CH_3\overset{*}{C}H_2I \xrightarrow[3.\ H]{1.\ Mg,\ 2.\ CO_2} CH_3\overset{*}{C}H_2CO_2H \xrightarrow[P]{Br} CH_3\overset{*}{C}HBrCO_2H$$

$$\xrightarrow{NH_3} CH_3\overset{*}{C}HNH_2CO_2H$$

<u>Alanine-3-C^{14}</u>, $\overset{*}{C}H_3CHNH_2CO_2H$

$$\overset{*}{C}H_3I \xrightarrow{CH_3CONHC(Na)(CO_2C_2H_5)_2} CH_3CONHC(CO_2C_2H_5)_2-\overset{*}{C}H_3$$

$$\xrightarrow[2.\ HCl]{1.\ NaOH} \overset{*}{C}H_3CHNH_2CO_2H$$

As in the case of choline, the alanine will be used for metabolic studies of amino acids. Low activity material has been prepared; the major problem being studied now is the purification of the product.

<u>Experimental Chemistry.</u>

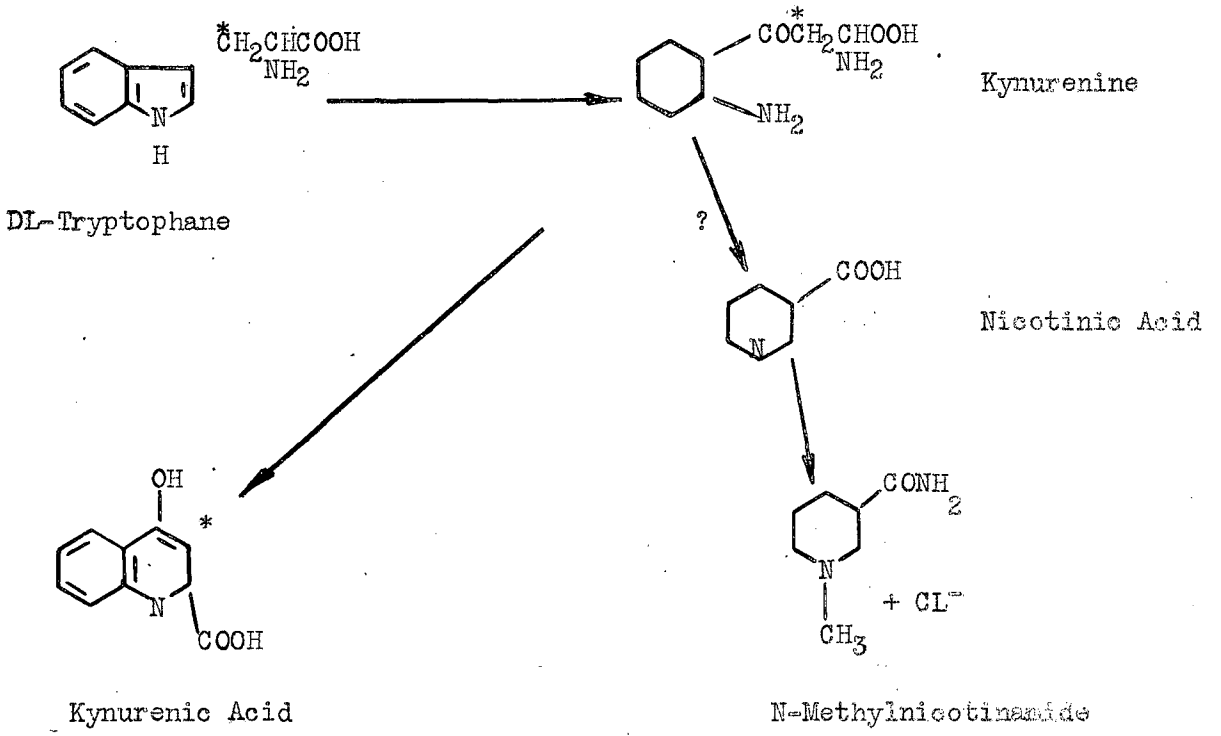
<u>Decarboxylation of Malonic Acid.</u> Malonic acid, synthesized from active KCN and dead chloracetic acid, has been decarboxylated with the hope of noting an isotope effect; such an effect was detected. Assume that carboxyl-labeled malonic acid can lose carbon dioxide by two paths only, one resulting in production of inactive carbon dioxide and the second resulting in radioactive carbon dioxide. The first process involves the rupture of a C^{12}-C^{12} bond while the second takes place at the C^{12}-C^{14} link. If these two bonds differ in strength, or if the activation energy for the decarboxylation process is affected by the presence of an heavy isotope in the carboxyl group, an amount of radioactivity different from one-half the original total label should be found in the carbon dioxide. By analogy with known processes occurring in deuterium-labeled compounds, the C^{12}-C^{14} bond should be ruptured less frequently than a C^{12}-C^{12} bond in the same position.

The carboxyl-labeled malonic acid was decomposed by heating at its melting point. The experiments were carried out in a 1-2.2 millimole scale. The experiments show that out of one hundred decarboxylation events approximately forty-five involve rupture of a C^{12}-C^{14} bond. Thus, the relative frequencies of C^{12}-C^{12} and C^{12}-C^{14} rupture are $\frac{55}{45}$ or 1.22 instead of $\frac{50}{50}$ or 1.00 which would be the case if rupture of either bond was equally probable. The figures just quoted are based on the ratio of specific activity of carbon dioxide and malonic acid for four experiments. When the calculation is based on the ratio of carbon dioxide and acetic acid activities, the frequency rate is $\frac{47}{53}$ or 1.13. These experiments are to be repeated on a larger scale in order that the difference between the acetate basis and carbon dioxide basis values can be resolved. Experiments are also to be carried out on various substituted malonic acids.

Biological Chemistry

Biochemical studies have been made in three fields: (1) the metabolism of C^{14}-labeled tryptophane, an essential amino acid, (2) the metabolism of C^{14}-labeled tyrosine and C^{14}-labeled dihydroxyphenylalanine (Dopa) and (3) the metabolism of C^{14}-labeled dibenzanthracene, a carcinogen.

Tryptophane. The preparation of DL-tryptophane-β-C^{14} has been discussed in a previous progress report. The mechanism of the mammalian conversion of tryptophane into kynurenine, kynurenic acid, and nicotinic acid has been studied in rabbits, dogs, and rats.



The kynurenine and kynurenic acid isolated from the urines were radioactive, and by degradation the label was found to be in the methylene and in the 3-position, respectively. From these data it was formulated that the kynurenine is formed from tryptophane by direct opening of the pyrrole ring, and the kynurenic acid by direct ring-closure from kynurenine. The N-methylnicotinamide was not radioactive, indicating that it was produced from the tryptophane by some method other than ring-closure to a quinoline derivative followed by oxidation.

The position of the label in the kynurenine (sp. act., 114 counts/min/mg.) was proved by its conversion by means of alkaline hypoiodite to iodoform (sp. act., 81 counts/min/mg; calc'd. 78), which could only have originated from the methylene carbon atom. The kynurenic acid (sp. act., 143 counts/min/mg.) was decarboxylated thermally to give inactive carbon dioxide. It was also oxidized to o-carboxyoxanilide (sp. act., 125 counts/min/mg, calc'd 130) which was hydrolyzed to five oxalic acid (sp. act. as calcium oxalate, 188 counts/min/mg; calc'd. 198) and was also decomposed thermally to give radioactive carbon dioxide (sp. act. as $BaCO_3$ 129 counts/min/mg; calc'd 128) and inactive carbon monoxide. Formylanthranilic acid, the probable intermediate in this decomposition, liberates carbon monoxide on heating. These reactions strongly indicate, but do not absolutely prove, that the labeled carbon atom is in the 3-position of kynurenic acid.

Tyrosine and Dihydroxyphenylalanine (Dopa). The distribution of activity in the tissues of mice bearing melanoma following administration of DL-tyrosine-β-C^{14} by stomach tube has been investigated to compare the results obtained by this method of administration with the pattern obtained when tyrosine is given intravenously. The data show that the distribution is not greatly changed. There is the same rapid rise and fall in the specific activity for the exhaled carbon dioxide and a similar rapid rise and fall in the activity of the excreta. The exhaled carbon dioxide reaches its peak of activity in about one hour; at the end of twelve hours about 15 percent of the administered activity has been eliminated in the breath and about 30 percent in the excreta. The relative activity of the tissues was about the same as in the intravenous injection experiments. The adrenals, intestines, kidneys, liver, lymph nodes, tumor, and thyroid comprise the group of most active tissues. The blood plasma also showed a high activity.

An experiment has been carried out to determine whether the pattern of activity distribution in mice bearing melanoma is significantly different in the early period (one-half hour) following injection of labeled DL-tyrosine from the later pattern (12 to 72 hours after injection). It was of particular interest to see whether the rapid initial excretion is paralleled by a rapid initial rise in tissue activities. The results show that the tissues take up activity very rapidly; the specific activities are nearly as high one-half hour after injection as they are after 12 hours. The relative distribution pattern is about the same as that observed in the later (12 to 72 hour) interval. The urine and intestinal contents showed a very high specific activity. The rapidity with which this activity appears suggests that some of it is unchanged tyrosine, perhaps predominantly the D form.

In order to determine whether the activity in the tissues was firmly bound, an animal was perfused with Tyrode's solution. Little or no activity was washed out of the tissues. This does not necessarily mean that all the tyrosine had been incorporated into the protein, but it does show that in one-half hour, the administered tyrosine had been fixed and had entered into the metabolic process and was not merely circulating in the tissue fluids. This is an additional indication that the activity distribution observed in the tissues after intravenous administration does not reflect nonphysiological processes resulting from the momentary flooding of the animal with the amino acids when the injection is made.

Dibenzanthracene. In further investigations on the metabolic degradation in the mouse of 9,10 dibenzanthracene-9-C^{14}, the acidic fractions from the feces have been studied. Chemical experiments with the radioactive material indicate that carboxylic acids were present and that synthesized products were hydroxy-and polycarboxylic acids.

Some radioactive carbon dioxide was obtained on working up the feces which showed that the molecule must be cleaved oxidatively in the body and to some extent in the middle of the molecule. Accordingly, the following compounds, which seem to be good guesses as to the metabolic degradation products of dibenzanthracene, were added to the acidic solution to see if they would carry the radioactivity: α naphthoic acid, β naphthoic acid, 1,2, naphthalic acid, 5-hydroxy-1-naphthoic acid, 5-hydroxy-2-naphthoic acid, benzoic acid, and phthalic acid. None of these compounds carried activity, and hence must be excluded as degradation products.

The feces from five hundred mice given dibenzanthracene by stomach tube are being processed so that it may be possible to isolate the compounds in a reasonable amount and thus identify them.

Photosynthetic Chemistry

Mechanism of Photosynthesis. In the study of photosynthesis, which is the process whereby green plants utilize light energy and carbon dioxide for growth and production of plant material, the administration of $C^{14}O_2$ to green algae under a variety of conditions has continued. Work has progressed from the identification of radioactive materials produced during dark fixation by previously illuminated algae to the identification of the products formed in short periods of photosynthesis, i.e., the very first products of photosynthesis. Dark fixation of the $C^{14}O_2$ was studied at first, since the number and nature of radioactive products was limited by the supply of reducing energy in the plant. Photosynthetic (i.e., in the light) fixation has now been shown to produce the same intermediates with similar distribution of C^{14} in the molecules. The results with the algae Scenedesmus are given in the following table:

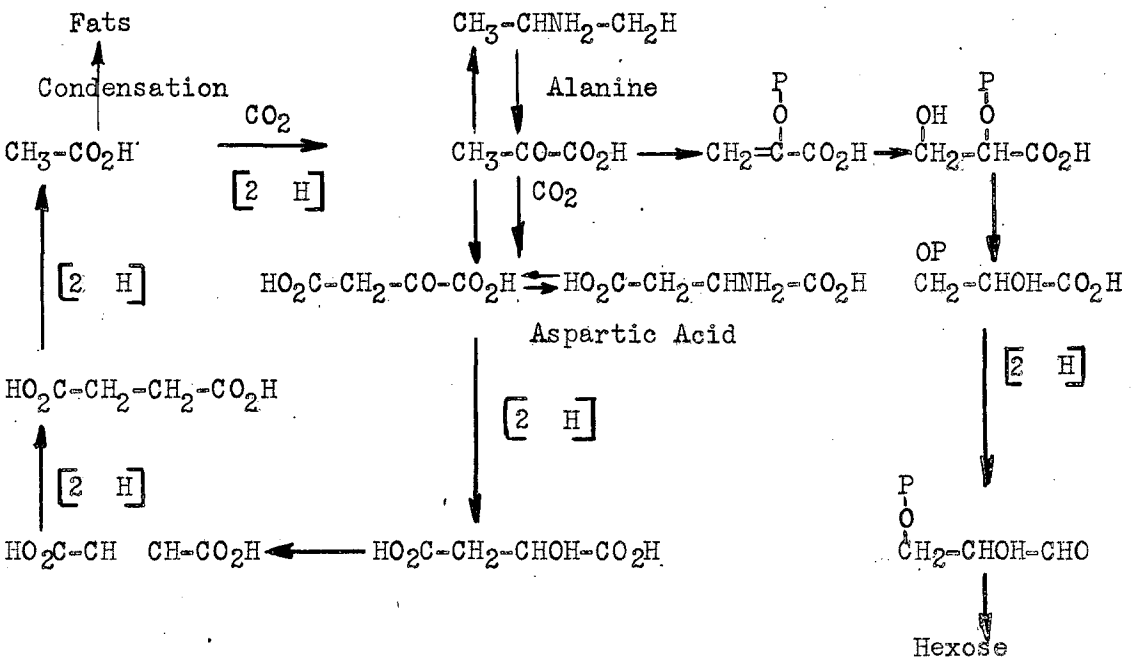
CO_2 FIXATION BY SCENEDESMUS

		10 min. Preillumination 1 min. Dark Fixation	30 second Photosynthesis	60 second Photosynthesis
Analysis of Cell Material % of Fixed Activity	Total Activity Fixed/cc. cells (c.p.m. x 10^{-6})	0.97, 100%	6.2, 100%	12, 100%
	Insoluble	0%	0%	5%
	I. Ether Extract at pH 1	12%	10%	3.7%
	II. Amino Acids	39%	11%	3.7%
	III. A Sugar Phosphates	4.2%	44% { 2% III-A, 97% III-B, 0.5% IV }	59% { 29% III-A, 54% III-B, 15% IV }
	III. B Phosphoglycerate	42%	27%	20%
	IV. Sugars	0.1%	4.7%	4.1%

The major difference between the dark fixation of carbon dioxide listed in the second column and the photosynthetic products listed in the third and fourth columns is found in Fraction III-A, the ammonia eluate of products adsorbed on the anion exchange resin. It is believed that the light energy stored by the preilluminated algae is insufficient to produce a large amount of the compound which appeared in III-A. Thus, Fraction III-A from the photosynthesizing algae has been found to be broken down by re-adsorption on the ion exchange column followed by re-elution. The apparent oxidation or conversion of III-A to material appearing in III-B which has been identified as phosphoglyceric acid indicates that III-A contains phosphoglyceraldehyde or some similar compound. Work on the identification of these compounds is continuing.

The amino acids synthesized in both the light and dark experiments have been shown to be similar. They have been separated using paper chromatography and identified

as 3- and 4-carbon amino acids by radio autographs of the paper chromatograms. In all cases, aspartic acid and alanine are the major radioactive amino acids, while β-alanine, serine, asparagine, and phenylalanine possess slight radioactivity. The fact that no radioactive glutamic acid is found demonstrates that the tricarboxylic acid cycle is not involved. The mechanism given below shows the relationship of the intermediates of photosynthesis which has been identified in this laboratory.



Since the relationship of carbon dioxide partial pressure to dark fixation by preilluminated plants has remained in some question, the carbon dioxide pressure dependence of dark fixation has been measured. The result is very similar to that found for the steady state photosynthesis, and the hundred fold increase in the initial slope of the curve for preilluminated algae over that for the predark algae strongly precludes the possibility of fixation by reversal of decarboxylation reactions.

The Function of Acetic Acid in Photosynthesis. The relationship of acetate to photosynthesis has been studied by a series of feeding experiments using Chlorella, Scenedesmus, and tobacco leaves. Since glucose is one of the major products of photosynthesis, the incorporation of acetate into the plant growth scheme should be demonstrable by isolating the glucose and some indication of the mechanism obtained by degradation of the sugar. Thus, the feeding of carboxyl-labeled acetate could produce the following labeled glucoses: (1) the combination of acetate and carbon dioxide to pyruvate and the condensation of two pyruvate molecules would give glucose labeled in the 2 and 5 positions; (2) carboxyl-labeled acetate condensing by the tricarboxylic acid cycle should give glucose labeled in the 3 and 4 postions; (3) direct condensation of two acetate molecules would produce a 3,4 labeled glucose.

A suspension of Scenedesmus was allowed to photosynthesize in the presence of carboxyl-labeled acetate for 30 minutes. The sugars from this solution and comparable solutions kept in the dark were isolated and degraded. In a typical distribution of activity of sugar formed in the light, 57.7 percent was in the 3,4 position, 21.4 percent was in the 2,5 position, and 20.9 percent in the 1,6 position. In the sugar synthesized in the dark 59.3 percent of the activity was in the 3 and 4 carbon atoms, 21.6 percent in the 2 and 5 carbon atoms, and 15.1 percent in the 1 and 6 carbon atoms.

When acetate was added to cell suspensions of Chlorella or Scenedesmus all the

material which entered the cells was fixed in non-volatile compounds. In 30-minute photosynthesizing periods, 50-85 percent of the activity was present in non-water soluble cell material. The radioactive material was also nonether soluble and did not become water or ether soluble by acid hydrolysis. After treatment with ethanolamine, the radioactive material was soluble and ether-extractable. Acetate (0.005M) when added to the cell suspensions of Scenedesmus showed no inhibiting or accelerating effect on either respiration or photosynthesis.

Chlorophyll and Photosynthesis. Experiments designed to test whether chlorophyll transfers non-labile hydrogen during photosynthesis are almost concluded. The experimental procedure consisted in the suspension of Chlorella algae in D_2O followed by the exposure of a vessel to light for a time of such duration that the mole ratio of oxygen evolved as the result of photosynthesis to chlorophyll present was 20-1; identical runs without light were also made. The chlorophyll was then isolated, purified and analyzed for deuterium content. The procedure used was applicable only to non-labile hydrogen, since exchange with hydrogens capable of transfer would proceed to the same extent regardless of the presence or absence of light and the isolation and purification of the chlorophyll would result in a loss of all exchangeable deuterium by virtue of copious washing with ordinary water. Thus, the scheme that has been tested is as follows:

$$\text{Chlorophyll} \longrightarrow \text{dihydrochlorophyll (photochlorophyll)} + 2H$$

$$\text{Photosynthesized chlorophyll} + HOH \longrightarrow \text{Chlorophyll} + O_2$$

The result of the initial experiments showed more deuterium in chlorophyll from algae exposed to light than in those kept in the dark, but the ratio of deuterium incorporated was still only one-quarter of that expected. Later work confirmed earlier experiments and noted that in four to five hour reactions the ratio of deuterium incorporated in the chlorophyll in the light to the deuterium taken up in the dark was approximately 4. Some chlorophyll was apparently formed in the dark. This was further confirmed by the use of C^{14}. The ratio of the percent incorporation of C^{14} in the light-synthesized chlorophyll to the dark-synthesized chlorophyll indicates that the greater amount of deuterium in the light-synthesized chlorophyll could be accounted for by the formation of newly synthesized chlorophyll. The degradation of light and dark chlorophyll to smaller units (pheophorbide) which should still contain the active hydrogen and, therefore, give a higher analytical result showed no preferential distribution of deuterium within the prophin ring (as compared to phytol).

Analytical methods of conversion of combusted H_2O-D_2O to hydrogen-deuterium were shown to be satisfactory. Control exchange experiments with pure chlorophyll in 90 percent acetone, 10 percent deuterium water showed the usual number of labile hydrogens. The results of the experiments are, therefore, negative in character and indicate that (a) chlorophyll may act as a sensitizer rather than as a hydrogen transport agent or (b) if it does not act as a hydrogen carrier then it (1) functions via an enolizable hydrogen, or (2) the fraction of chlorophyll that is fairly active is small compared to the amount of material, or (3) the path of hydrogen from water to chlorophyll proceeds via a large reservoir of non-exchangeable hydrogen.

II. Quarterly Progress Report. Project 48B.

W. M. Latimer, Director

Metals and High Temperature Thermodynamics

Thermodynamics of CN and CH. Work is continuing on the determination of the heat of formation of CN by the same method used previously on C_2. Not much progress has been made during the last three months due to lack of time available for work. The furnace is being remodeled to allow its extension to temperature approaching 4000°K. by replacement of the graphite tube by a TaC tube and by use of porous carbon and graphite for the insulation and radiation shields. It is hoped that these changes will allow the determination of CH as well as the determination of the emission probabilities of some of the species present in the sun.

Thermodynamics of Gaseous Halides. A new apparatus has been built to simplify determination of the volatilities of metals in $HCL-H_2$ gas streams. The volatility of molybdenum is being studied now. The previous data on the volatility of copper are being compared with spectroscopic data. There is some indication that a dimer Cu_2Br_2 may exist in addition to CuBr and Cu_3Br_3 even though no evidence for a dimer could be found in the chloride system where CuCl and Cu_3Cl_3 appear to be the only species. More study of the bromide system may be warranted. Comparison of the data with spectroscopic data is difficult since the heat of sublimation of copper is not known accurately enough. It may be necessary to determine this quantity.

Thermodynamics of Gaseous Oxide and Hydroxides. Most of the preliminary work on the solid phases has been completed and work will start soon on the determination of the volatilities of metals and oxides in H_2O-H_2 gas streams. Also the Knudsen effusion method will be used to determine the stability of gaseous oxides such as TiO, MgO, AlO, and SiO. A report summarizing the thermodynamics of the solid oxides has been completed.

Refractories. In addition to the continuing work on carbides, studies of several silicide systems were made. X-ray patterns for several lower phases in the Ta, W, Ti, Mo, Zr systems were found, but the structures appear to be complicated and have not been worked out yet. The silicides may be very useful refractories.

Liquid Metal Systems. The work of running cooling curves for Na-Bi-U alloys is continuing, but no definite conclusions can be given yet. The work on the heats of formation of Na-Sn and Li-Sn alloys has been completed. A new high temperature calorimeter is being built to allow more accurate determinations of heats of high temperature reactions.

Structure of Solids. Lattice energy calculations and other theoretical studies are being made to learn more about the type of binding in the solid state, particularly for nitrides, carbides, sulfides, and oxides.

Basic Chemistry, Including Metal Chelates.

Extraction Experiments with Uranium (VI). The series of experiments previously described has been completed and extended. The distribution coefficient of uranium(VI) between dilute acid and benzene solutions of TTA has been measured over a range of concentrations. The results confirm the fact that uranium(VI) occurs as an ion with a positive charge of two in acid concentrations of from 0.001 to 2.0 molar. The apparent deviations indicated by the work of E.L. King are not confirmed.

Analysis for uranium has been performed by measuring the absorption spectra of the various solutions. This has necessitated the measurement of the molar extinction

coefficients of the various molecular species present, and a study of the equilibria between them. In aqueous solution at high TTA concentrations uranyl ion is complexed by the negative ion of TTA giving UO_2K^+, where K^- represents a TTA molecule from which a hydrogen ion has been removed. Under the conditions of the extraction experiments only a very small amount of this species is formed.

In benzene the principal uranium species is the chelate, UO_2K_2, and the corresponding second power dependence of the extraction coefficient on TTA concentration has been verified. An additional species exists in benzene. It may be written as $UO_2K_2 \cdot HK$, involving an additional molecule of TTA. Its formation accounts for the previously observed but unexplained large decrease in the activity coefficient of uranium(VI) chelate, UO_2K_2, in benzene solutions of increasing TTA concentration.

It has been estimated from the distribution observed with macrozirconium that the extraction coefficient for zirconium should be about 1.4 in the experiments with the coated vessels. The same amount of zirconium tracer was added to all vessels so the loss of zirconium to the wall surfaces could be compared. The results are as follows:

1. The extraction coefficient obtained with the glyptal coated flask was 1.06. The combined amount of zirconium in the aqueous and benzene phases in arbitrary units was 3890.

2. The extraction coefficient was found to be 1.26 in the flask which had been coated with "dri-film". The amount of zirconium in the two phases expressed in the same arbitrary units was 4230.

3. The collodion coated flask gave an extraction coefficient of 0.73 and the combined amount of zirconium in solution was 4300.

It is apparent from the above data that the "dri-film" coating was the most satisfactory, however the extraction coefficient is still about 10 percent lower than the estimated value calculated from the macro experiments.

Further work is now in progress to determine the causes of the discrepancy between the macro and tracer experiments.

Lanthanum Complexes. Recent work on the chelate complexing of lanthanum has been retarded due to considerable contamination of strontium and yttrium activities in the shipment of radioactive barium and lanthanum received from Oak Ridge. It was necessary to subject this material to a purification process. The resulting lanthanum tracer, when used in extraction experiments, gave irreproducible results. A new shipment of barium and lanthanum has just been received and the experiments will be repeated.

Zirconium Chemistry. In the study of the distribution of zirconium between perchloric acid and benzene-TTA solutions two undesirable effects have been noticed. First, the extraction coefficients of duplicate experiments performed at the same time in exactly the same manner may differ from each other by as much as 15 percent. The second effect is that the overall extraction level with trace amounts of zirconium is not as great as it should be as calculated by the measured distribution of macro amounts of zirconium. Since these two effects are present, any precise chemistry of zirconium which is studied by means of the TTA-extraction procedure is subject to question, and therefore it is desirable to find the causes of these effects.

It has been mentioned previously that all chemicals employed in the TTA work have been repurified. The only chemical which has not been repurified is perchloric acid. Since perchloric acid is rather difficult to purify and since the original stock was one which had been previously double distilled by the manufacturer, a different source of the acid was used. Experimental data obtained from experiments

with the new stock retained all the undesirable effects as noted above.

The extraction experiments which have been performed since the repurification of the chemicals have been directed so as to shed some light on two possible causes for the irreproducibility and the low extraction levels obtained with tracer zirconium. It is believed that radiocolloid formation as well as complex ion formation may be responsible for these two effects. Therefore several series of experiments have been performed as follows. Zirconium tracer was equilibrated with 2 M $HClO_4$ and 0.01113 M TTA in benzene. After equilibrium was reached, the aqueous phase was transferred to a new flask containing a fresh 0.01113 M TTA-benzene solution. This solution was shaken until equilibrium was established, and then the aqueous phase transferred as before. It was found that after the aqueous phase had been transferred two of three times, the extraction coefficient had dropped to about one-half its original value. The final aqueous phase was then removed and placed in a "Visking" cellulose casing and ultra filtered. The result showed that about 20 percent of the zirconium tracer could not pass through this membrane thus suggesting that this amount of tracer was radiocolloidal. However this amount of radiocolloid can not entirely account for the decrease in the extraction coefficient. This, of course, requires the assumption that the pores of this cellulose casing are small enough to prevent all radiocolloid from passing through the membrane.

Various experiments have been performed using glass vessels which were coated with different substances to prevent the zirconium from coming into contact with the glass surface. Those coatings that have been tried are the following:

1. Glyptal coated with "dri-film"
2. "Dri-film" ($SiOCl_2$)
3. Collodion coated with "dri-film"

SECRET

SECRET

DECLASSIFIED

SECRET