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I. QUARTERLY PROGRESS REPORT. Project 48

A. Nuclear Chemistry

G. T. Seaborg and I. Perlman

Mass Assignments in the Rare Earth Region

Maynard Michel

The four rare earth elements lutetium, ytterbium, thulium and erbium have been produced in high yield by spallation of tantalum with 340 Mev protons and the isotopes produced, including several not previously reported, have been investigated with the object of establishing the decay characteristics and the correct mass assignment.

The principal attack was to collect the individual isotopes using the time-of-flight mass spectrometer. However, an examination of the decay curves indicated a rather complex mixture of isotopes, so a preliminary survey of the active isotopes was made using the conventional 60° sector type mass spectrograph. The reason for this decision was that the time-of-flight machine, as set up now, can collect only 4 isotopes from a given run, making a preliminary knowledge of the approximate mass numbers very useful.

Results are now available from the 60° sector type machine for ytterbium, erbium and thulium. All samples were run on a simple thermal ion source, using a tungsten ribbon as the emitting surface. The samples were mounted in the form of sulfates and collection made on Ilford G-2 photographic plates. Immediately after each run the master plate was placed face to face with an Eastman III-0 spectroscopic plate in order to make a transfer of lines due to radioactive isotopes. Several transfers were made, at varying times, from each master plate in order to determine relative half-lives to some degree.

The gross ytterbium decay shows periods of 68 minutes, 62 hours and 31 days, with a 7 hour growth superimposed. The mass spectrograph transfer indicated active isotopes at mass 166 and 169, with half-lives consistent with assignment to the 62 hour and 31 day activities, respectively. Both these isotopes have been reported previously and our results are in agreement with the previous assignments.

For thulium, the gross decay indicates periods of 7.7 hours, 9.6 days, 26 hours and one considerably longer at low yield. The 26 hour has not been reported previously. The transfer plates from 2 runs indicate active isotopes at masses 165 and 167 only. These are consistent with assignment to the 26 hour and 9.6 day activities, respectively. No line was seen at mass 166, although the plates were sufficiently fogged that no significant lower limit can be set on the yield. However, the 7.7 hour activity has been assigned by genetic relationships as will be shown later.

For erbium, the gross decay indicates period of 3-1/4 hours, 29 hours and 9.4 days. The previously reported 10 hour decay was evidently not resolved but it has been obtained by milking thulium from the same bombardment. The transfer plates give three active isotopes at masses 160, 161 and 165. The first two can be assigned to the 29 hour and 3.25 hour activities, with some doubt attached to the 3.25 hour line since it does not seem to decay fast enough. The line at 165 also seems to be much too long lived to be the 10 hour isotope and not long enough to be 9.4 days. No line was seen at mass 169, but the yield of the longer lived isotope was considerably below the others and might not be expected to show up. Considerable doubt can be attached to the proper assignment of the 3.25 hour and 10 hour erbium isotopes, with the possibility of the existence of isomers not too unlikely.

No successful runs have been made on lutetium as yet.

It is now planned to collect samples of each of the isotopes produced, in the time-of-flight spectrometer to get accurate assignments and decay periods. Recent difficulties with the ion source have slowed the program but work is again under way.

Two successful runs on ytterbium have been made in the time-of-flight machine in which Yb^{166} was collected in appreciable quantities. These samples (~300-500 counts per minute) show a 7.2 hour growth and a 59 hour decay, confirming the assignments of both Yb^{166} and Tm^{166}.

Work on the erbium and thulium isotopes is now in progress.

The Crystal Structure of High Cyclobutane

D. H. Templeton

According to Rathjens and Gwinn,[1] cyclobutane melts at 182° K and has a transition point at about 145° K. We have investigated the structures of the two solid forms by the x-ray diffraction method.

Samples provided by Dr. Rathjens were sealed in Pyrex capillaries, mounted in the camera, and cooled in the usual way with a stream of cold nitrogen gas. Powder patterns of the low temperature form contain many lines. The structure is not cubic and has not been solved. Powder patterns of the high form show only a single line which is assigned to 110 on the basis of the single crystal work.

Slow freezing resulted in single crystals of the high form whose orientations seemed to be random in the capillary. Rotation photographs of four such crystals at about 173° K [axes of rotation approximately (100), (3$\bar{1}$1), (53$\bar{1}$), and (44$\bar{1}$), respectively] show the unit cell to be body-centered cubic with

1. G. W. Rathjens and W. D. Gwinn, to be published.

$a = 6.06 \pm 0.03$ A (λ Cu Kα = 1.542 A). Though only reflections of the forms (110) and (200) are observed, the interpretation is unique because the crystals were misaligned enough to permit independent observation of "coincident" reflections in nearly every case so that the multiplicites of the forms were determined. The distribution of the spots among the various layer lines was also checked in each case. This unit cell, with two molecules, corresponds to a calculated density of 0.84 ± 0.01 g cm^{-2}.

If the origin is chosen at the center of gravity of one molecule, then the second molecule must be at the body center. To achieve cubic symmetry, these molecules must have rotational disorder, either static or dynamic. Structure factors were calculated on the basis of complete spherical symmetry, using molecular dimensions consistent with the electron diffraction results of Dunitz and Schomaker[2] for the gas. No correction was made for temperature or absorption. The results, listed in Table I, explain the rapid decrease of intensity with increasing Bragg angle and the absence of the higher order reflections. However, it is impossible to get perfect agreement with the observed ratio of F(110) to F(200) unless the absorption error is more serious than is estimated. This fact is interpreted as evidence that the rotational disorder is not spherically symmetric. Indeed, since the intermolecular distance, 5.25 A between centers, is substantially smaller than the largest van der Waals diameter of cyclobutane, the rotations are expected to be hindered appreciably.

These data yield no information concerning the planarity of the carbon skeleton, since reasonable deviations from planarity have a trivial effect on the form factor of the rotating molecule.

TABLE I

Structure Factors for High Cyclobutane

hkl	F_{obs}	F_{calc}
110	2.8	2.8
200	1.5	1.0
211	<0.9	<0.2

The Crystal Structure of TbOF

D. H. Templeton and Carol H. Dauben

TbOF was prepared by Darrell Feay and B. B. Cunningham. It was made by pyrohydrolysis of TbF_4 at 400° C in a muffle furnance overnight. It is rhombohedral, isostructural with the rhombohedral form of YOF and LaOF.[1] The lattice parameters determined from a powder photograph taken with chromium Kα radiation (λ = 2.2909 A) are:

$$a = 6.750 \pm 0.010 \text{ A}$$
$$\alpha = 33.1 \pm 0.1^{\circ}$$

2. J. D. Dunitz and V. Schomaker, J. Chem. Phys. 20, 1703-7 (1952).

1. W. H. Zachariasen, Acta Cryst. 4, 231 (1951).

Furnace Spectrum of Plutonium

John G. Conway

The spectrum of plutonium is being investigated using a vacuum furnace of a modified King type. A tantalum tube containing the plutonium is inserted into the hot zone and the spectrum is then observed out the end of the tube. The work to date has yielded several plates in the wave length range of 3400 Å to 6000 Å and a temperature range from 2100° C to 2600° C. Spectra are still being taken hence no wave length measurements or temperature classification of the plutonium lines have as yet been attempted.

Development of Vapor Pressure Apparatus

B. B. Cunningham and S. C. Carniglia

A symmetrical twin Knudsen effusion device has been constructed for the measurement of vapor pressures of the heaviest elements and their compounds in the region 10^{-5} to 10^{-2} mm Hg. Alpha particle counting will be employed to determine the number of molecules effusing down a defined beam to a receiver.[1] The twin design will facilitate the simultaneous investigation of two substances at a few points, establishing accurate relative values of their vapor pressures by minimizing inadvertent differences in the temperatures at which comparisons are made. The equipment is easily adapted, also, to measurements on a single substance.

The tantalum effusion vessel is heated by a molybdenum resistance-wire furnace, powered by low voltage alternating current. Sensibly uniform chamber temperatures have been obtained from room temperature to a maximum of about 1500° C. In-place calibration of a Pt-90 Pt, 10 Rh thermocouple against standard melting points is now in progress.

Radiation Chemistry

Amos S. Newton

The data on the helium ion radiolysis of alcohols[1] has been extended and the yield values checked for better accuracy and consistency. In Table I are presented the yield values of hydrogen and hydrocarbons for all alcohols through the butyls. These data show well the regularities point out by McDonnel.

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1. Of the numerous papers describing the general techniques, see for example: T. E. Phipps, R. L. Seifert and O. C. Simpson, Argonne National Laboratory Classified Report CN-3223 (September 1945).

1. W. R. McDonnel, University of California Radiation Laboratory Report, UCRL-1378, Thesis (Ph. D.) (June, 1951).

TABLE I

Yields of Hydrocarbons Produced in the Helium Ion Bombardment of Alcohols

Product	Yield, G (Molecules/100 ev)							
	Methyl	Ethyl	n-Propyl	Iso-Propyl	n-Butyl	Iso-Butyl	n-Sec. Butyl	Tert. Butyl
H_2	3.46	3.46	2.80	2.71	3.59	2.77	2.61	1.24
CH_4	0.36	0.43	0.067	1.14	0.055	0.142	0.37	1.60
C_2H_2	-	0.040	0.035	0.019	0.027	0.013	0.050	0.014
C_2H_4	-	0.17	0.30	0.022	0.090	0.022	0.38	0.091
C_2H_6	0.014	0.17	0.54	0.17	0.035	0.017	0.86	0.52
C_3H_6	-	0.003	0.140	0.27	0.21	0.81	0.051	0.020
C_3H_8	-	0.025	0.145	0.088	0.46	0.65	0.110	0.017
Isobutene	-	$\ll$0.001	0.010	~0.007	-	0.067	-	0.27
Butene-1				-	0.093	-	0.053	-
Butene-2							0.126	
Isobutane	-	-	-	~0.04	-	0.162	-	0.11
n-Butane	-	<0.010	0.100	-	0.127	-	0.216	-

Other correlations can now be made with these data. In the compounds methyl, isopropyl, tertiary, butyl and isobutyl alcohols there is no obvious method for the production of ethane other than the reaction of methyl radicals.

One can write simple kinetic equations for the formation of methane and ethane in the process,

$$CH_3 + H \longrightarrow CH_4 \qquad dN/dt(CH_4) = k_1(CH_3)(H) \qquad (1)$$

$$CH_3 + CH_3 \longrightarrow C_2H_6 \qquad dN/dt(C_2H_6) = k_2(CH_3)^2. \qquad (2)$$

Thus the ratio of methane to ethane formed depends upon both the concentration of hydrogen and methyl radicals. With helium ion bombardments of the intensity in the range used in these experiments, estimations indicate that each helium ion can be considered as a separate chemical event, in which case the concentrations are constant and independent of the rate of bombardment. Hence, concentrations can be measured by the total yield of products found and radical concentrations can be estimated from the products formed by reactions of these radicals.

$$(CH_3) = |CH_4| + 2|C_2H_6| \qquad (3)$$

$$(CH) = 2|H_2| + |CH_4| + |C_nH_{2n+2}|_{n>2} \qquad (4)$$

Such formulations assume a knowledge of mechanisms and the ultimate fate of such radicals, and, if k_1 and k_2 are considered to be rate constants, the assumption is implied that other reactions (e.g., $H + H \longrightarrow H_2$) are slow compared to reactions (1) and (2). A safer assumption is to say that competing reactions are included in the formulation defining k_1 and k_2 and that these are relative rate constants. In any case one can then set up the expression:

$$\frac{|CH_4|}{|C_2H_6|} = \frac{k_1(CH_3)(H)}{k_2(CH_3)^2}, \qquad (5)$$

and letting $K = k_1/k_2$,

$$K = \frac{|CH_4|\,(CH_3)}{|C_2H_6|\,(H)}. \qquad (6)$$

The result of such a calculation of K is shown in Table II and it is seen that of the alcohols studied K is constant at 1.3 except for a marked discrepancy for isobutyl alcohol. The yield of both methane and ethane is small in this case, as expected, since the methyls are not attached to the carbinol carbon atom. However, there appears to be about 5 times too much ethane for the amount of methane produced. (Compare qualitatively the relative yields from methyl alcohol.) It is thus apparent that either 1) our formulation is breaking down and many methyl radicals are disappearing to other fates, or 2) ethane is being produced by another process, e.g., a rearrangement. Since no rearrangement which might produce ethane is obvious either from structural considerations or an analysis of the mass spectrometer fragmentation data of isobutyl alcohol, the problem is still open to question.

The question immediately arises as to whether such a formulation might be general in helium ion bombardments of liquid systems. Data previously presented[2] on di-isopropyl ether gives a value of K = 1.26 and runs on acetone and acetic acid gave 1.20 and 1.11, respectively. The results on acetic acid do not include the methyl radicals going to form acetone, which product was shown to be formed though not quantitatively measured. Hence, K for acetic acid is low by an unknown amount. Since the group of compounds studied is such that wide variations in the ratio of H_2-CH_4-C_2H_6 were found, it is encouraging that the value of K shows such a constant value.

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2. A. S. Newton, University of California Radiation Laboratory Quarterly Report, UCRL-1878, (July 2, 1952), pp 28-31.

TABLE II

Alcohol	Yield, G, of Product or Radical						K
	CH_4	H_2	C_2H_6	C_nH_{2n+2}	(CH_3)	(H)	
CH_3OH	0.36	3.46	0.014		0.39	7.28	1.38
$(CH_3)_2CHOH$	1.14	2.71	0.17	0.09	1.48	7.65	1.30
$(CH_3)_3COH$	1.60	1.24	0.52	0.13	2.64	6.19	1.31
$(CH_3)_2CHCH_2OH$	0.142	2.77	0.017	0.81	0.176	6.49	0.23

In the above experiments, data were obtained on the gaseous products formed in the helium ion radiolysis of acetone and acetic acid. See Tables III and IV. Although a complete analysis was not made for products not found in the vapor phase, the results might be of interest to others and are hence tabulated here. The acetic acid used was reagent grade glacial acetic dried by boiling with triacetyl borate followed by distillation. The melting point of the final material was 16.67° C (Lit. 16.68°C). The acetone used was dried by refluxing with calcium metal and distillation. The second quarter of the distillation though a 35 plate column was used for bombardment.

TABLE III

Some Chemical Products Formed in the Helium Ion Bombardment of Acetic Acid

Product	Experimental G	Literature[3] G
H_2	0.52	0.85
CO	0.38	0.5
CH_4	1.38	1.05
C_2H_6	0.84	0.2
CO_2	4.04	2.9
CH_3CHO, $CH_3\text{-}C(=O)\text{-}CH_3$, $CH_3\text{-}C(=O)\text{-}OCH_3$	Present in small amounts in gas.	
H_2O (in liquid)	2.15	-

3. W. L. Whitehead, C. Goodman and I. A. Breger, J. Chemie Physique 48, 184 (1951). Solid acid bombarded with radon alpha particles.

TABLE IV

Some Chemical Products Formed in the Helium Ion Irradiation of Acetone

Product	G
H_2	0.91
CO	0.80
CH_4	0.89
C_2H_2	0.03
C_2H_4	0.04
C_2H_6	0.53
CH_3-C≡CH	>0.006
C_3H_6	0.03
C_3H_8, CH_3CHO	0.02
CO_2	0.03
iC_4H_8	0.003
"Polymer"*	0.79

* Calculated as acetone from weight of material not volatile in vacuum.

Tantalum Spallation and Fission

W. E. Nervik

During the past quarter the decay characteristics of isotopes of the heavy rare earths produced in the bombardment of tantalum with 349 Mev protons were investigated.

The gross rare earth fraction was first separated from other spallation and fission products and purified by repeated fluoride and hydroxide precipitations. The individual rare earths were then separated on a Dowex-50 cation exchange resin column. Preliminary experiments indicated that on a column 43 cm long with a diameter of 14 mm packed with 4 percent cross linked Dowex-50 resin of mesh size 300-400 a satisfactory separation could be effected with an eluting solution which was 0.43 molar in total lactate, 0.01 molar in phenol, and at a pH of 3.35. With the column maintained at an

elevated temperature by trichloroethylene vapor and with a flow rate of 0.5 milliliter/minute, the individual rare earths were eluted in the following times: lutetium, 177 minutes; ytterbium, 199 minutes; thulium, 244 minutes; erbium, 307 minutes; holmium, 379 minutes. A rough sketch of the elution curve is given in Fig. 1.

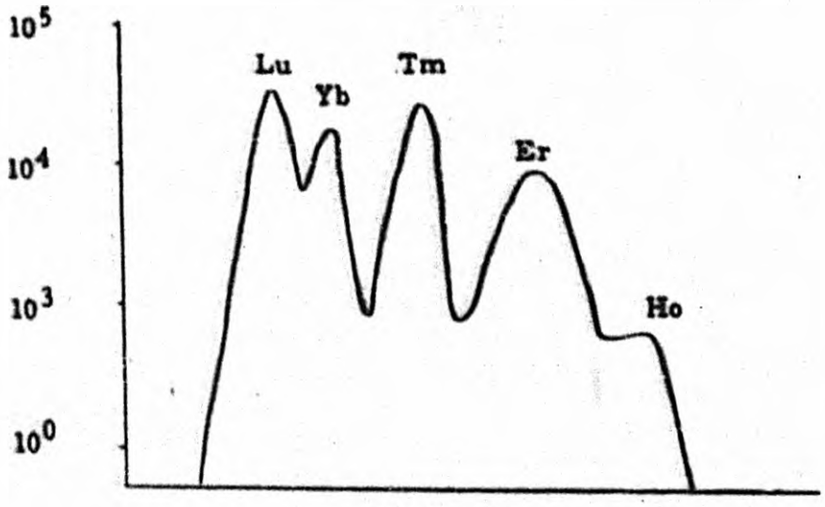

Fig. 1

Gross decays of aliquots taken at the peaks of the elution curve are being followed. Analysis of the decay curves is not complete as yet but several facts are apparent from data obtained up to the present time.

Lutetium. The shortest lived isotope seems to have a half-life of approximately one hour rather than the four hours reported.[1]

Ytterbium. Yb^{166} has been reported[1] to have a half-life of 62 hours. This activity has been isolated with the ytterbium fraction, separated on a time-of-flight mass spectrograph and identified definitely as belonging to Yb^{166}. Growth of the 7.7 hour Tm^{166} daughter was observed and the Yb^{166} decayed with a half-life of 59.5 hours.

A short lived activity with a half-life of 68 minutes was also observed in the gross ytterbium fraction decay. Milking of thulium from ytterbium after this activity had been allowed to die out gave large amounts of 7.7 hour Tm^{166} and 9.6 day Tm^{167}. Since Tm^{166} has been shown to be the daughter of 59.5 hour Yb^{166} the 68 minute ytterbium activity is tentatively assigned the mass number 167.

1. J. M. Hollander, I. Perlman, G. T. Seaborg, Table of Isotopes, UCRL-1928 Revised, December, 1952.

Thulium. Gross decay of the thulium fraction indicates the presence of 7.7 hour Tm^{166}, 9.6 day Tm^{167}, plus longer lived activities which are probably Tm^{168}, Tm^{170} and Tm^{171}. In addition, there is a previously unreported activity which seems to have a half-life of approximately 26 hours. Attempts to isolate this activity have been unsuccessful but a milking experiment performed four days after the initial separation on the day of bombardment gave reasonable amounts of pure Er^{165} which decayed with a 10.2 hour half-life. On the basis of this experiment the new activity is assigned mass number 165. Its half-life is quite uncertain, however, since the parent Tm^{165} and its 10 hour daughter growth had to be resolved from fairly large amounts of 7.7 hour and 9.6 day thulium activities. It seems reasonable to state that the half-life is of the order of a day.

Erbium. The erbium fraction presents by far the most confused picture of any of the elements investigated. Previously reported[1] neutron deficient isotopes of erbium are: $Er^{160-161}$, approximately 17 hours; Er^{163}, approximately 65 hours; Er^{165}, 10 hours. Decay of the gross erbium fraction indicates the presence of two activities; one of 3.25 hour half-life, and the other 29 hours. Separation of the isotopes on a conventional mass spectrograph and use of the photographic plate transfer technique indicate that the short lived activity belongs to Er^{161} and that Er^{160} and Er^{165} are present in equal abundance and have approximately the same half-life. Combined with the fact that 10 hour Er^{165} has been milked from Tm^{165}, these data indicate that Er^{160} should have a half-life of approximately 29 hours, Er^{161} approximately 3.25 hours, and Er^{165} should have an isomeric state which decays with a half-life of approximately 29 hours. No Er^{163} activity was seen on any of the photographic transfer plates.

Attempts are being made at the present time to isolate each of the nuclides of interest on the time-of-flight mass spectrograph in order to identify the mass numbers without doubt. The most recent experiments indicate that this has been done with some success although detailed information is not yet available for publication.

Spallation Products of Silver

Per Kofstad

Studies have been continued on the spallation of silver with 340 Mev protons. All elements between cadmium and iron with the exception of krypton and technetium have been isolated and the cross sections for the formation of some sixty isotopes have been evaluated. The cross sections range from about 100 mb for silver to 10^{-3} mb for copper. In the region of the periodic table below copper, we have isolated sodium, magnesium, chlorine, manganese, cobalt and nickel with cross sections close to 10^{-3} mb for all of them. As a comparison, Luis Marquez found the cross sections of Be^{7} and F^{18} to be 10^{-1} and 10^{-2} mb, respectively.[1,2] These values will be checked later.

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1. L. Marquez and I. Perlman, Phys. Rev. 81, 953 (1951).
2. L. Marquez, Phys. Rev. 86, 405 (1952).

A short-lived activity which has not been reported previously in the literature has been found in the niobium fraction from the spallation of silver. The half-life is 2 hours, decaying partly by positron emission, the positron having an energy of 2.9 Mev as determined by a crude beta ray spectrometer. From cross section considerations and assuming Nb^{90} to be a 100 percent β^+ emitter, this activity is estimated to decay 50 percent by positron emission. Zirconium was milked after 24 hours of separation from niobium; the zirconium fraction gave a positron activity with a half-life of 78 hours which was assigned to Zr^{89}. The short-lived niobium activity is thus assigned to Nb^{89}.

Decay of Am^{242}

T. Passell

The gamma ray conversion electron spectrum of 16-hour Am^{242m} has been observed using the double-focusing beta ray spectrometer. Seven peaks were observed which could be assigned to 2 gamma rays of 43.4 kev and 41 kev, respectively; the former in its electron capture decay to Pu^{242} and the latter in its beta decay to Cm^{242}.

Previous workers had proposed a third gamma ray and assigned it to an isomeric transition in Am^{242}. Our interpretation allows it to be present but in smaller abundance than we were able to detect. This interpretation is consistent with data obtained on the same isotope with a bent crystal gamma ray spectrometer.

The Entropies of Aqueous Species

James W. Cobble

Empirical considerations of entropy have led to the correlation of the entropies of aqueous solutes with the charge, interatomic distances (or molar volumes) and the structure of the species. Such correlations have yielded equations for the calculation of the absolute entropies for any ion or neutral species and should prove useful in the thermodynamics of aqueous solutions. The results of the investigations are contained in UCRL reports 2103, 2104 and 2105.

Theoretical considerations of the proper model for the solute-solvent interaction consistent with the above equations are in progress.

Complexing of the Lanthanides and Actinides

James W. Cobble

Investigations are currently being initiated on the complexing of lanthanide and actinide ions using standard and Raman solution spectroscopy and potentiometry. Identification and characterization of such complex ions may be of interest with regard to the recent proposals on "f" electron bonding in the actinides. Similar characterizations are also being considered for the "yl" type ions with a view to understanding the special stability of the uranyl ion.

The Chemistry of Technetium and Rhenium

James W. Cobble

A number of estimated thermodynamic functions for technetium and rhenium compounds have proved useful in describing the chemistry of these two elements and these values, together with a review of the chemistry of technetium, are being published in a symposia issue of the Journal of Physical Chemistry.

B. Bio-Organic Chemistry

M. Calvin and A. A. Benson

Observations on the Radiation Decomposition of Some C^{14}-Labeled Compounds

B. M. Tolbert, P. T. Adams, Edward L. Bennett, Ann M. Hughes
Martha R. Kirk, R. M. Lemmon, R. M. Noller, R. Ostwald and Melvin Calvin

The work described here was initiated by a recent observation that considerable radiation decomposition has occurred to a sample of choline-methyl-C^{14} chloride which had been synthesized in these laboratories last spring. This observation, together with a similar one made by Dr. Sidney Weinhouse on samples of C^{14}-labeled calcium glycolate which were synthesized here four years ago, has illustrated the need for information on the rate of decomposition of C^{14}-labeled organic compounds. Since this group has carried out during the past six years the syntheses of several dozen labeled organic compounds, we have available a number of such compounds which could be examined for evidence of radiation decomposition. From these compounds we picked a list of twelve which had been exposed to large amounts of self-radiation since their syntheses and for which there are unequivocal data to show their high degree of purity at the time of synthesis. All of these compounds had been stored in dry, solid form in a dark cabinet at room temperature. The extent of the radiation decomposition was established by making paper chromatograms of each of the compounds and determining, by means of radioautographs of the chromatograms, if other radioactive constituents had appeared during storage. Similar paper chromatograms had been prepared at the time of synthesis and in all cases there had been no observable (or, at most, less than one percent) radioactive impurity. By comparing the old radioautographs with the ones recently prepared, we have measured the percentage of radioactive impurities which have appeared since the time of synthesis. In the case of choline, which had been stored in an evacuated sealed tube, we were able to determine the amount of a volatile radioactive product, namely, trimethylamine, which had formed during storage. None of the other compounds were stored in sealed tubes and any volatile decomposition products would not be detected unless they comprised a considerable fraction (at least ten percent) of the radioactivity of the freshly prepared compound. The data which were obtained are summarized in Tables I and II.

The data of Tables I and II show that there is a general relationship between the amounts of radiation (Reps) and the likelihood of finding some radiation decomposition; however, the choline and stilbamidine provide two major exceptions. Our data are too scanty to permit predictions as the the susceptibility of various organic groups to radiation damage - this we hope to do later with the accumulation of further information. For the present, however, it should be emphasized that users of C^{14}-labeled compounds would be well advised to check the purity of their compounds frequently, particularly if the compound is of high specific activity and/or was prepared several years ago. For checking such purity, paper chromatography provides a very convenient tool, especially for finding non-volatile radioactive impurities. However, it may also be useful for volatile impurities if these compounds have either a basic or acidic function and can be kept in a non-volatile form on a paper chromatogram by using, respectively, an acidic or basic solvent (for example, the chromatography of choline which is reported here). There are several references in the literature[1, 2, 3, 4] to the use of paper chromatography for determining the purity of radioactive preparations.

TABLE I

Compounds Showing More than One Percent Radiation Decomposition

Compound	Date Prepared	Sp. Act. (μc./mg.)	Reps[a] x 10^{-6}	No. of non-volatile Radioactive Products Observed on Paper Chromatograms[b]	% Decomposition
Valine-4,4'-C_2^{14} · HCl	Nov. 1951	6.0	10	1	1-2
Norvaline-3-C^{14}· HCl	Jan. 1951	17.7	46	6	5
Norleucine-2-C^{14}	March 1952	17.4	20	4	2
Choline-methyl-C_1^{14} chloride	May 1952	13.0	11	0[c]	63
Calcium glycolate-1-C^{14}	Feb. 1949	5.8	30	1	13[d]
Calcium glycolate-2-C^{14}	Feb. 1949	4.0	21	1	22[d]
Cholesterol-4-C^{14}[e]					

(a) These values were calculated as follows:

$$\text{Roentgens equivalent physical (Reps)} = \frac{(k)\,(N)\,(\bar{E})\,(\text{Reps/ev})}{\text{wt. in grams}}$$

where: k = fraction of radiation absorbed (arbitrarily given the value of 1 in our calculations)

N = total number of events since the time of synthesis

$\bar{E}$ = average energy of the radiation (=50,000 ev. for C^{14})

Reps/ev is taken as 1.9×10^{-14}

(b) These observations were made in February 1953.

Footnotes, Table I (continued)

(c) The Main decomposition product of the methyl-labeled choline is the volatile trimethylamine. Further details are recorded in the experimental part of this paper.

(d) These values were determined (private communication) by Dr. Sidney Weinhouse who found that radioactive formate was present in these percentages. The formic acid was steam distilled from the glycolic acid and its radioactivity measured as CO_2 after oxidation by mercuric ion.

(e) Considerable radioactive decomposition of cholesterol-4-C^{14} has been observed by Prof. William G. Dauben (private communication). These observations will be described in detail in a separate publication.

TABLE II

Compounds Showing Less than One Percent Radiation Decomposition

Compound	Date Prepared	Sp. Act. (μc./mg.)	Reps x 10^{-6}
Glycine-2-C^{14}.HCl	Dec. 1951	4.9	6
Guanine hydrochloride-4-C^{14}	March 1950	2.6	9
8-Azaguanine-4-C^{14}	March 1950	3.8	13
Adenine sulfate-4,6-C_2^{14}	March 1950	2.9	10
8-Azaadenine-4,6-C_2^{14}	March 1950	4.4	15
Stilbamidine diisethionate-amidine--C_2^{14}	Feb. 1951	13.7	31
Thyroxine-α-C^{14}	May 1950	1.0	3
Succinic acid-2-C^{14}	Dec. 1949	3.9	14

Experimental

The valine-4,4'-C_2^{14}, norvaline-3-C^{14}, and norleucine-2-C^{14} which were found to show radiation decomposition were all prepared via an acetamidomalonate synthesis using as starting materials, respectively, isopropyl-methyl-C_2^{14} iodide, propyl-1-C^{14} iodide and butyl-1-C^{14} iodide. All of these preparations will be the subject of a forthcoming publication. The final purification of the labeled compounds was accomplished by elution from an ion-exchange column. Paper chromatography of the preparations (phenol-water in one direction, butanol-propionic acid-water in the other) showed that there was less than one percent of radioactive impurities present.

The preparation of the labeled choline has been reported earlier.[5] The material described here was prepared at a later date (May 1952) using the same procedure. The later preparation included, in addition, the same paper chromatographic search for radiochemical impurities as was carried out on all the labeled compounds mentioned in this report. Again, these impurities were less than one percent of the preparation.

Since the radiation decomposition of the choline is so extensive (63 percent) we made some efforts to determine what the principal decomposition products were. Upon opening a sealed tube of the choline a pronounced odor of acetaldehyde was observed. The presence of acetaldehyde was established by the preparation directly, from the choline sample dissolved in water, of the 2,4-dinitrophenylhydrazone. This derivative, after recrystallizations once from glacial acetic acid and twice from ethanol, was found to have a melting point of 146° (literature value[6]: 147°). It was also found to be completely non-radioactive.

About two-thirds of the radioactivity of the original choline preparation was volatile - it was lost in the operation of making a plate for counting the choline chloride. That this volatile product is trimethylamine was demonstrated as follows: (1) Alkali was added to a freshly opened tube of the choline and the volatile products were collected in a connected trap which contained a saturated solution of picric acid in ethanol and which was cooled in a liquid nitrogen bath. The trap was removed, closed off from the atmosphere and warmed, with shaking, to about 60°. After the trap was cooled back to 0°, crystalline picrate appeared. The solvent was removed by filtration and the precipitate was dried. Its melting point after two recrystallizations from ethanol was 211° (literature value[7]: 216°) and its activity was 1.67 mc./mmole (the activity of the original choline chloride was 1.82 mc./mmole; both values determined by direct plating). (2) When the labeled choline chloride from a freshly opened tube was placed in acid solution and an aliquot portion paper chromatographed (one-dimensionally) using a n-butanol-conc. HCl-water (4:1:1 by vol.) solvent, two radioactive spots were obtained. The faster moving spot (higher R_F value) contained 63 percent of the total activity and the slower moving spot (choline) contained 37 percent of the activity on the paper. The faster moving spot was cut out, eluted, and the material co-chromatographed with labeled trimethylamine hydrochloride. These materials proved to be chromatographically identical (one-dimensional paper chromatogram with the same acidic butanol solvent.

The syntheses of the labeled glycolic acids, and the criteria for their purity at the time of preparation, have been described in an earlier publication.[2] The same applies to the guanine, 8-azaguanine, adenine and 8-azaadenine[8], to the glycine[9], to the succinic acid[10] and to the stilbamidine[11]. The thyroxine synthesis (R. M. Lemmon, unpublished work) was carried out using glycine-2-C^{14} and following the original procedure of Harington.[12]

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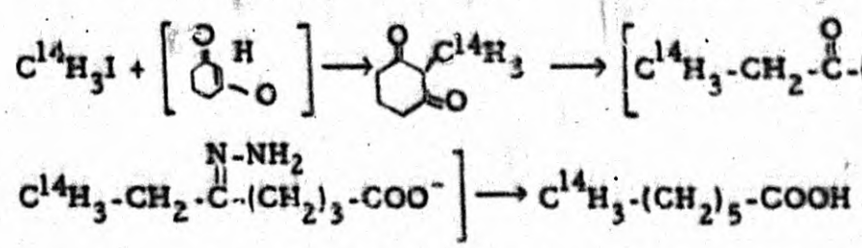
Syntheses of Labeled Organic Compounds

Synthesis of Heptanoic-7-C^{14}-Acid. R. M. Moller

Sodium heptanoate-7-C^{14} has been prepared (following, in general, the procedure of H. Stetter and W. Dierichs, Berichte 85, 61 (1952)) by condensing methyl-C^{14} iodide with the potassium salt of dihydroresorcinol, splitting the resultant 2-methyl-C^{14}-cyclohexane-1, 3-dione with base, and reducing the resultant keto-acid with hydrazine. The reaction sequence is outlined below.



The condensation was done in an aqueous media in a sealed tube; the molal ratio of potassium dihydroresorcinol to methyl iodide was 1.2 to 1. It was found that the concentration of the solution may be varied over a considerable range without greatly affecting the yield of the desired condensation product. The optimum concentration was found to be that which was sufficient for the "hydrated" potassium dihydroresorcinol to melt at a temperature below 65° and still be a solid at room temperature.

It was also found that the yield could be increased by lowering the reaction temperature. However, this involved a longer time for the reaction to go to completion. Boiling methanol was chosen as it provided a temperature (65°) giving an optimum yield in a reasonable length of time (4 hours).

The 2-methyl-C^{14}-dihydroresorcinol(2-methyl-C^{14}-cyclohexane-1, 3-dione) was isolated from the reaction mixture and excess potassium dihydroresorcinol by dissolving in a sodium hydroxide solution (1 eq. NaOH/ eq. of starting $C^{14}H_3I$), extracting with ether to remove any methyl-ethers and/or di-substitution products, and then acidifying to pH 5. The product, which is practically insoluble in water, was filtered, washed and dried.

The 2-methyl-C^{14}-dihydroresorcinol was dissolved in methanol and sufficient pre-prepared reduction solution was added so that the ratios of components were as follows: 1 mole of compound, 3.4 mole sodium hydroxide, 2160 ml of di-ethylene glycol and 135 ml of 85 percent hydrazine hydrate.

The mixture was brought to boiling and the low boiling components distilled out until the solution reached a refluxing temperature of 150°. After 2 hours, the low boiling components were again distilled out until the temperature of the solution reached 195°. The solution was refluxed at this temperature for 24 hours. The reduction mixture was then made acid and extracted with a benzene-ether solvent; the solvent was in turn extracted with a sodium hydroxide solution which was then made acid and the heptanoic acid steam distilled out.

On the radioactive preparation, starting with methyl-C^{14} iodide (2.21 g., 5.08 μc./mg.), the yield of 2-methyl-C^{14}-dihydroresorcinol was 45.1 percent and the subsequent overall yield of sodium heptanoate-7-C^{14} was 39.6 percent. It was found to contain no radioactive impurities (one dimensional paper chromatograms run in a propanol-ammonia solvent) and its specific activity is 4.79 μc./mg. (The theoretical value for the radioactivity is 4.74 μc./mg.)

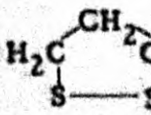
Studies on the Synthesis of Diethyl Malonate-2-C^{14}. Doris Chin

The synthesis of diethyl malonate-2-C^{14} has been investigated on a scale suitable for high activity preparations (15-20 mmoles). Preliminary experiments with inactive syntheses showed that malonic acid can be prepared easily and in high yield from chloroacetic acid via cyanoacetic acid and separated and purified as the calcium salt. Esterification was attempted by acidifying calcium malonate suspended in excess ethanol and refluxing 6 hours or more; the yields were about 30 percent. A synthesis of diethyl malonate from chloroacetic acid via ethyl cyanoacetate was tried but gave low yield of an ambiguous product containing nitrogen. The product could not easily be purified since ethyl cyanoacetate and diethyl malonate have very similar physical properties (boiling point, solubilities). The most promising method seems to be esterification by reaction of silver malonate with ethyl iodide; this preparation has given us yields of 75-87 percent based on silver malonate. Future work will study this method of synthesis in inactive and moderately active runs starting from sodium acetate and preparing chloroacetic acid, silver malonate and, finally, diethyl malonate.

Studies on the Synthesis of S^{35}-Labeled 6,8-Dithio-octanoic Acid

P. T. Adams

The synthesis of 6,8-dithio-octanoic acid ("thioctic acid")



H_2C CH_2 CH-$(CH_2)_4CO_2H$ labeled with radio-sulfur is being investigated. Two possible synthetic routes to this compound have been under consideration and the work done on each of these routes will be described separately below.

(a) The first attempts to prepare the thioctic acid were directed toward a synthesis through the intermediate compound $HC \equiv C\text{-}CHOH(CH_2)_4CO_2Et$. Adipaldehydic ester ($OCH(CH_2)_4CO_2Et$) was prepared in the following manner: Equal-molar quantities of adipic acid and diethyl adipate (prepared as directed in Org. Syn., Coll. Vol. II, p. 264, J. Wiley and Sons, New York) were mixed and heated at 250° for five hours. The mixture was allowed to cool, filtered and subjected to distillation under reduced pressure. Ethyl hydrogen adipate (m.p. 28-29°, b.p. 130-132°/1 mm) was obtained in 35 percent yield, with almost quantitative recovery of unused di-acid and di-ester.

The mono-ester was treated with a 15 percent molar excess of re-distilled thionyl chloride, allowed to stand at room temperature for 1-1/2 hours and heated under reflux on a steam bath for 16 hours. The half-acid chloride of adipic ester was collected by vacuum distillation (b.p. 95-97/2 mm) in 85 percent yield.

Reduction of the acid chloride with hydrogen, using a Pd-$BaSO_4$ catalyst, was carried out according to the procedure of G. B. Brown, J. Org. Chem., 12, 160 (1946). The adipaldehydic ester was obtained in 65 percent yield by vacuum distillation (b.p. 68-74/1 mm. m.p. 2-4-dinitrophenyl hydrazone: 76-77° (corr.)). The product was stored at liquid nitrogen temperature because of its tendency toward rapid polymerization.

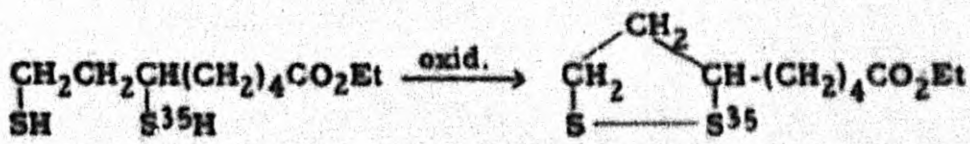
Condensation of this aldehyde with acetylene was attempted in two ways. Preparation of acetylene Grignard reagent in an atmosphere of excess acetylene, followed by addition of the aldehyde, gave only polymeric products. Condensation in sodium and liquid ammonia (K. Campbell, B. Campbell and L. Eby, J. Am. Chem. Soc. 60, 2883 (1938)), yielded mostly high-boiling polymers plus varying amounts of ethyl-hydrogen-adipate and ethyl-6-hydroxy caproate.

(b) A new synthetic route to the labeled thioctic acid is currently under investigation. The equations for this route are as follows:

$$ClOC(CH_2)_4CO_2Et + (CH_2)_2 \xrightarrow[2)\ distill]{1)\ AlCl_3} CH_2{=}CH{-}CO(CH_2)_4CO_2Et \xrightarrow{CH_3COSH}$$

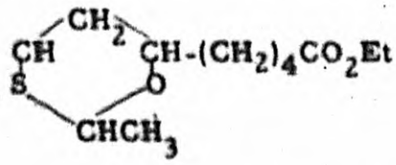
$$CH_3COSCH_2CH_2CO(CH_2)_4CO_2Et \xrightarrow{NaBH_4} CH_3COSCH_2CH_2CHOH(CH_2)_4CO_2Et$$

$$\xrightarrow[SO_2Br]{Pyridine} CH_3COSCH_2CH_2CHBr(CH_2)_4CO_2Et \xrightarrow[2)\ OH^-\ hydrolysis]{1)\ S^{35}{=}C(NH_2)_2}$$



The vinyl ketone has been prepared in the following manner: (M. W. Bullock, et al., J. Am. Chem. Soc. 74, 3455 (1952)). Dry aluminum chloride (1 mole) was added to 300 ml. of nitrobenzene cooled in an ice bath. To this solution, 0.5 mole of the acid chloride was slowly added. Ethylene was bubbled through the solution for four hours at a rapid rate and the solution was then poured onto a mixture of ice and chloroform. The organic layer was separated, washed with water and sodium bicarbonate, dried with sodium sulfate, and distilled. Hydrogen chloride was evolved during the distillation of the solvents. The vinyl ketone (b.p. 97-102/0.2 mm) was obtained in 35 percent yield.

In preliminary experiments, addition of thioacetic acid to this compound, followed by reduction with sodium borohydride, seemed to give rise to a product which is not the desired thio ester. However, there are indications that the compound produced may be the thio-acetal



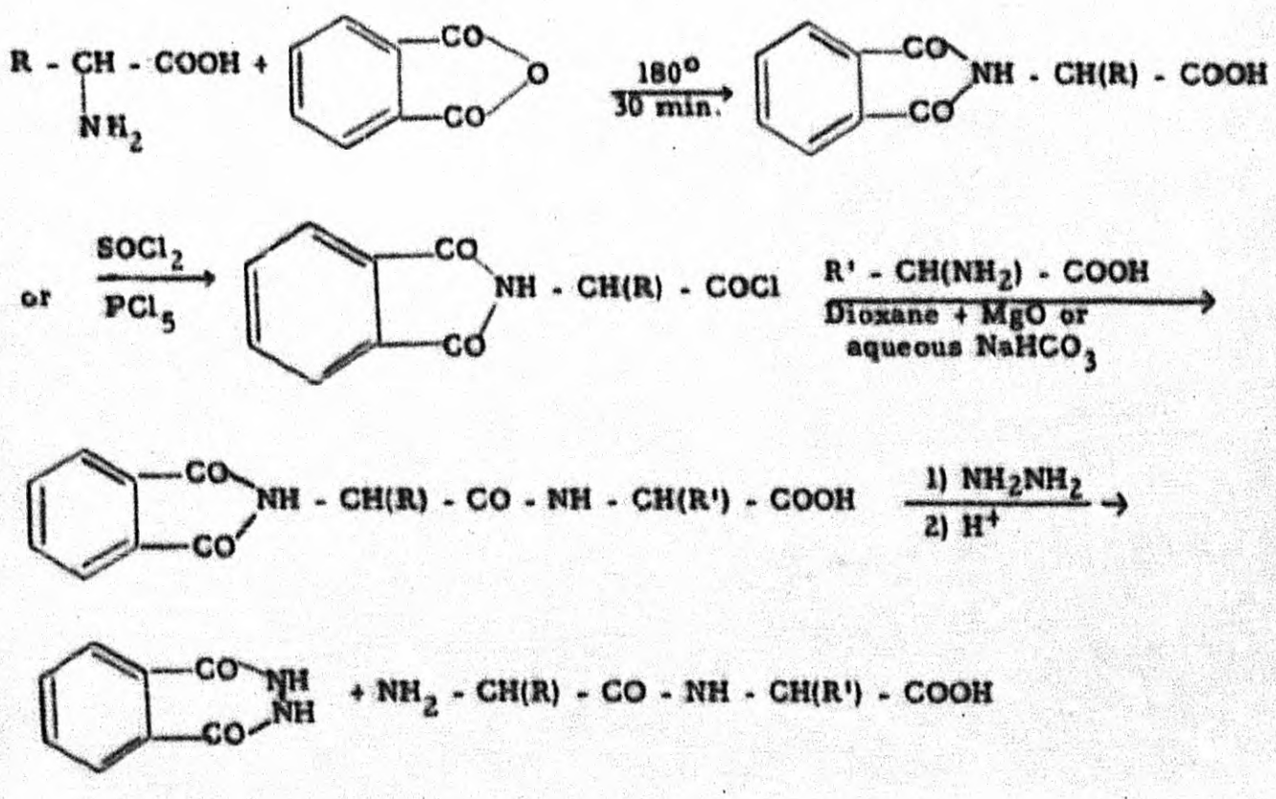
If this acetal is indeed the primary product, it may be found to be as useful an intermediate as the thiol ester, since the functional groups are still found on the desired carbon atoms.

Studies on the Syntheses of C^{14}-Labeled Peptides

R. Ostwald

As a preliminary step in an investigation of the mechanism of protein synthesis in living organisms, the synthesis of C^{14}-labeled peptides has been undertaken. Two methods of synthesis of peptides have been tentatively explored. These methods, and the results so far obtained, will be described separately below.

(a) The phthalyl method, as described by J. C. Sheean (J. Am. Chem. Soc. 71, 1856 (1949)) and W. Grassmann (Ber. 83, 244 (1950)), utilizes the following sequence of reactions:



Phthalylalanine was obtained in 86 percent yield, m.p. 160-161°. Phthalyl-alaninyl chloride was obtained as a glass in about 85 percent yield by either heating phthalylalanine in dry benzene with an equimolar amount of PCl_5 and evaporating to dryness, or by heating phthalylalanine with an excess of thionyl chloride and removing the excess reagent by repeated evaporation with chloroform. The second procedure seems less satisfactory because of the difficulty in removing the last traces of thionyl chloride.

Condensation of the acid chloride with L-leucine to give phthalyl-alanyl-L-leucine was tried in two different ways:

(1) Phthalyl-alaninyl chloride dissolved in dioxane was dripped slowly into an ice-cold, stirred suspension of leucine and MgO. After acidification and evaporation of the solution, the gummy solid was extracted with ethylacetate to separate the product from $MgCl_2$. This procedure proved to be unsatisfactory because the inorganic salt could not be separated completely and because the product obtained constituted only a small percentage of the expected yield.

(2) When phthalyl-alaninyl chloride dissolved in chloroform was condensed with leucine in an aqueous solution of $NaHCO_3$, and the resulting mixture acidified with acetic acid, evaporated to dryness and taken up in alcohol, 55 percent of the leucine was recovered as such. The phthalyl-alanyl-leucine could not be obtained in crystalline form, but remained an oil or dry gel.

In another experiment the alkaline condensation mixture was acidified with hydrochloric acid instead of acetic acid and extracted with boiling alcohol to remove the NaCl. Some leucine was recovered, but the phthalyl-alanyl-leucine remained an oil. One-dimensional paper chromatography in butanol-propionic acid solvent indicated that this oil contained large amounts of leucine, some phthalylpeptide and phthalylalanine.

Hydrolysis of this oil by heating with hydrazine hydrate in alcohol and subsequent acidification with acetic acid, yielded phthalylhydrazine (45 percent of theoretical, assuming the oil to have been only phthalylpeptide and phthalylalanine) and a solid containing large amounts of alanine, some leucine and some peptide, as determined by paper chromatography. To determine the effect of this hydrolysis procedure on a peptide, glycyl-leucine was treated with hydrazine as described above. One- and two-dimensional paper chromatograms showed that a large amount of the peptide is cleaved to give leucine.

(b) E. Fischer's method for the synthesis of peptides (Ber. 40, 1754 (1907)) is described by the following scheme:

$$R - CHBr - COBr + R - \underset{\displaystyle NH_2}{\underset{|}{CH}} - COOH \xrightarrow{NaOH} R - CHBr - CO - NH - CH(R') - COOH$$

$$\xrightarrow{NH_4OH} R - CH(NH_2) - CO - NH - CH(R') - COOH.$$

α-bromo-propionyl bromide and an equimolar amount of 1 N NaOH were alternately dripped into an ice-cold, stirred solution of L-leucine in 4 N NaOH. The yellow oil which precipitated upon acidification was extracted with ether. The water layer yielded 40 percent of the starting amount of leucine. The ether extract yielded an oil (presumably a mixture of α-bromo-propionyl leucine and α-bromopropionic acid). This was aminated using a mixture of $(NH_4)_2CO_3$ and NH_4OH at 55° for five hours. The product was purified on a Dowex 50 ion-exchange column to remove NH_4Br. It represented a 32 percent yield (calculated as peptide) and proved by paper chromatography to contain alanine, leucine and peptide.

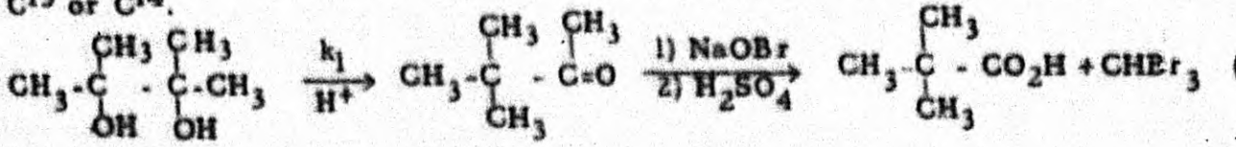
From these results it seems essential to find a method to separate alanyl-leucine from alanine and leucine. Using the phthalyl method, these amino acids are present in the end product because of the difficulty of obtaining pure phthalyl-alanyl-leucine, free from phthalylalanine (arising by hydrolysis from unreacted phthalyl-alaninyl chloride) and from unreacted leucine. The secondary difficulty is the hydrolysis of the peptide with hydrazine. This may possibly be overcome by the use of phenylhydrazine and equimolar amounts of the reagents rather than the excess used so far.

The Fischer method presents the analogous problem of obtaining pure α-bromopropionyl-leucine free of α-bromopropionic acid (which gives rise to alanine during amination) and of unreacted leucine. Fractional elution from an ion-exchange column and chromatography on Whatman No. 3 paper (this paper allows heavy loading) are being investigated as methods to separate the peptide from the contaminating amino acids.

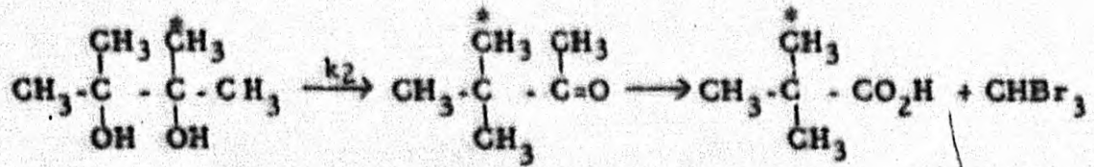
The Isotope Effect in the Pinacol Rearrangement

D. E. Pack

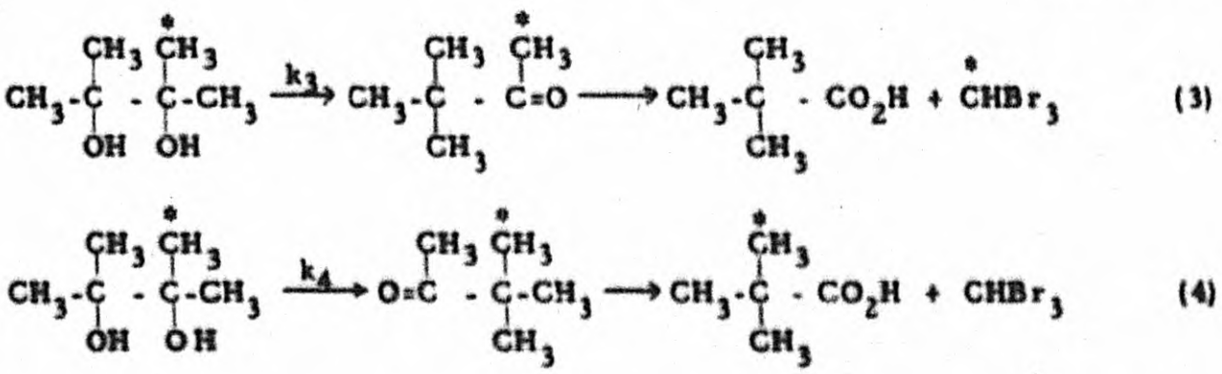
The purpose and preliminary results of this work were described in the Quarterly Progress Report, UCRL-1959, for June, July and August 1952. Since that time the method of calculation of the isotope effect has been re-examined. The rearrangement of pinacol and the splitting of the resulting pinacolone can be represented by the following equations, where C* represents C^{13} or C^{14}.



(1)



(2)



(3)

(4)

In the above equations and in the following calculations only the mono-labeled pinacol is considered, although the labeling is actually equal in all four methyl groups. Calculations show that the number of di-, tri- and tetra-labeled molecules is a very negligible fraction of the total.

Referring to the above equations and assuming that the reaction is first order with respect to pinacol and assuming that the bromoform reaction proceeds without any isotope effect, the specific activities or mole fractions of the trimethylacetic acid and bromoform are given by the following equations, where P, T and B refer to unlabeled pinacol, trimethylacetic acid and bromoform, respectively, and P*, T* and B* refer to the same compounds containing C^{13} or C^{14}.

$$\frac{T^*}{T^* + T} = \frac{k_2 + k_4}{k_7 + k_3 + k_4} \cdot \frac{P^* (1 - e^{-(k_2 + k_3 + k_4)t}}{P^* (1 - e^{-(k_2 + k_3 + k_4)t}) + P (1 - e^{-k_1 t})} \qquad (5)$$

$$\frac{B^*}{B^* + B} = \frac{k_3}{k_2 + k_3 + k_4} \cdot \frac{P^* (1 - e^{-(k_2 + k_3 + k_4)t})}{P^* (1 - e^{-(k_2 + k_3 + k_4)t}) + P (1 - e^{-k_1 t})} \qquad (6)$$

When the reaction is complete, $t = \infty$ and equations (5) and (6) become, after rearrangement:

$$\frac{k_3}{k_2 + k_4} = \frac{\frac{P^*}{P^* + P} - \frac{T^*}{T^* + T}}{\frac{T^*}{T^* + T}} \qquad (7)$$

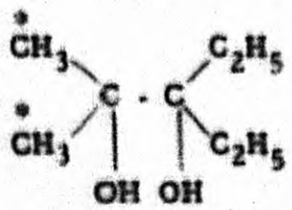
$$\frac{k_3}{k_2 + k_4} = \frac{\dfrac{B^*}{B^* + B}}{\dfrac{P^*}{P^* + P} - \dfrac{B^*}{B^* + B}} \qquad (8)$$

Combining equations (5) and (6) at any time gives equation (9).

$$\frac{k_3}{k_2 + k_4} = \frac{\dfrac{B^*}{B + B^*}}{\dfrac{T^*}{T^* + T}} \qquad (9)$$

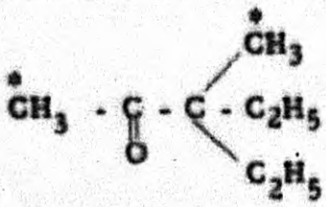
Thus it is seen that in the above derivation the ratio $k_3/k_2 + k_4$ is always obtained, although the ratio actually wanted is k_3/k_2. This result is not unexpected as an examination of equations (2) and (4) will show that the labeled trimethylacetic acid can arise by two different paths, one involving migration of $-C^{14}H_3$ and the other migration of $-C^{12}H_3$. At present, no method is known that will give the desired result with pinacol.

It might be added, in passing, that the use of an unsymmetrical pinacol such as 2-methyl-C^{14}-3-ethyl-2, 3-pentadiol-1-C^{14}



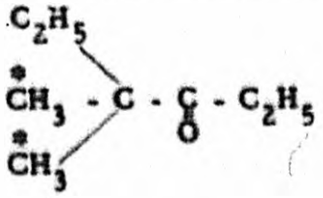
I

would obviate the above-mentioned difficulty. Two different products would be obtained from the rearrangement of the methyl group to yield



II

and the other migration of the ethyl group to yield



III

II being a methyl ketone will undergo the bromoform reaction to yield bromoform and diethylmethylacetic acid, while III will not react. In this way the two pinacolones can be differentiated and the desired rate ratio can be obtained. However, even if the desired results were obtained, a theoretical interpretation would be complicated due to the fact that the rearrangement involves not only the breaking of a carbon-carbon bond, but also the formation of a new bond which might be subject to an isotope effect itself. For these reasons the work is being discontinued.

Sodium Acetate Metabolism by Pantothenic Acid Deficient Rats

Martha R. Kirk and Ann M. Hughes

Production of Pantothenic Acid Deficient Rats

The production of pantothenic acid deficient rats has been previously reported (Unna, J. Nutrition, 20, 565 (1940)) and that procedure was followed in the present work. The diet used consists of purified casein (vitamin-free), fat (Primex), sucrose and Hubbell salts; which can be supplemented with vitamins as desired. In our experiments, the oil soluble vitamins and all the water soluble vitamins, except pantothenic acid, were added to the diet. Nursing females were started on the diet when the litter was fourteen days old. Young were weaned at the age of twenty-one days and continued on the diet. From each litter two young were selected as controls. These animals were raised separately and received the deficient diet plus pantothenic acid.

Elimination of Radioactivity in the Breath of Pantothenic Acid Deficient Rats Injected with Sodium Acetate-2-C^{14}

The metabolism of $C^{14}H_3COONa$, with and without injections of Coenzyme A, by the pantothenic acid deficient rats is being studied, using the apparatus previously described by us for measuring respiratory $C^{14}O_2$ (Quarterly Report, UCRL-1878, for March, April, May 1952). Acetate was injected intraperitoneally at the level of 2 mg (10 μc.) per rat. CoA, when used, was injected in the tail vein at the level of 3-4 mg per rat. The CoA used was obtained from Pabst Laboratories and is reported to be 65 percent pure. It was dissolved in normal saline and brought to pH 6-7 with 0.1 N NaOH. The metabolism of acetate by the control animals was also determined. In the experiments carried out thus far, the deficient rats metabolized acetate to

$C^{14}O_2$ slightly more rapidly without CoA than with the enzyme. The metabolism of the acetate by the control animals was similar to that of the deficient animals when the latter are given CoA. The greatest difference between the normal and deficient animals seems to be the production of a labeled compound other than $C^{14}O_2$ in the breath.

In previous experimental work involving our method of determining $C^{14}O_2$ (i.e., passing respired air through an ionization chamber), the chambers have shown no contamination at the end of a seven-hour experiment; that is, after conclusion of the experiment, the chamber is flushed with dry air for ten minutes, at the end of which time all activity will have been flushed out and the voltage on the electrometer will have returned to the base line. However, in the first experiment involving deficient rats, a large amount of activity remained in the chamber, even after flushing with dry air for several hours. This would indicate the production of some volatile metabolic compound other than $C^{14}O_2$ by these animals.

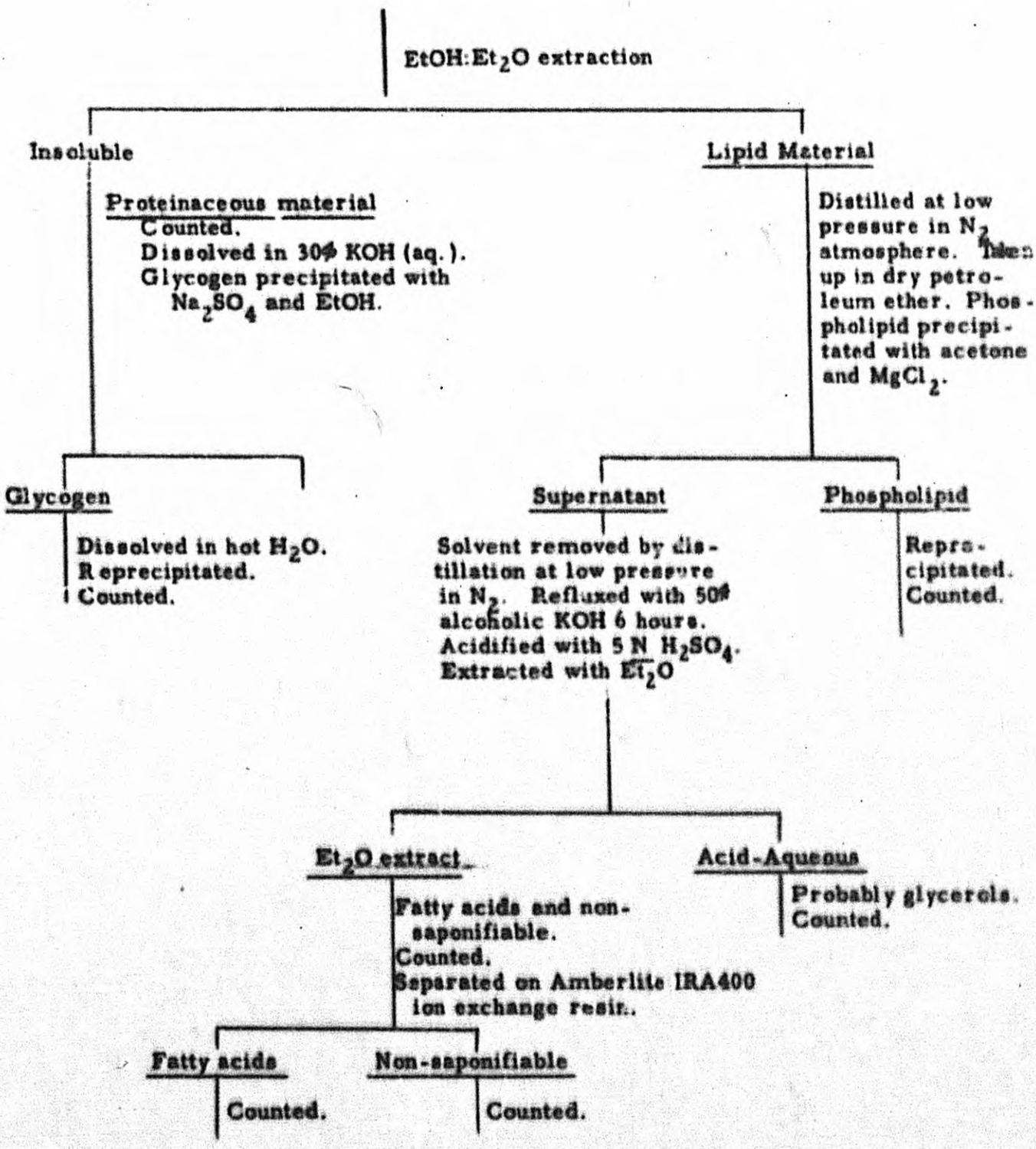
Attempted Identification of Volatile Compounds Other than $C^{14}O_2$ Exhaled by Pantothenic Acid Deficient Rats

A trap containing a few milliliters of concentrated H_2SO_4 was placed between the rat cage and ionization chamber and was found to remove the contaminant completely without removing any appreciable CO_2. Several methods of determining total activity in H_2SO_4 traps (including steam distillation and VanSlyke combustion) have been attempted and, while all show some activity present, none determines with accuracy the total amount in the trap.

Acetaldehyde was added to the separate H_2SO_4 samples from a number of different traps, each representing a different experiment. The 2,4-dinitrophenylhydrones were prepared and were each recrystallized from 95 percent ethanol to a melting point of 147°. In two of the cases, the derivatives were further purified by passing through a silicic acid column following the procedure of Roberts and Green (Ind. Eng. Chem., Anal. Ed., 18, 335 (1946)) and then recrystallized. In all cases the purified derivatives were radioactive, showing that at least one of the volatile compounds must be acetaldehyde. However, the data are as yet insufficient to permit us to say that acetaldehyde is the only radioactive carbonyl compound present in the H_2SO_4 traps.

Distribution of Radioactivity in the Livers of Normal and Pantothenic Acid Deficient Rats after Injection of Sodium Acetate-2-C^{14}

Experimental. One normal rat and two pantothenic acid deficient rats were each injected intraperitoneally with 2 mg (10 μc.) $C^{14}H_3COONa$. The normal rat and one deficient rat were sacrificed one hour after injection. The second deficient rat was sacrificed at the end of three hours. The livers were immediately homogenized with 95 percent ethanol and extracted in a Soxhlet apparatus with ethanol-ether (3:1 by vol.) for eight hours. The remaining separations were carried out according to the following scheme:



Activity of each fraction was determined by direct plating onto a platinum dish and counting in a Tracerlab Flow-Geiger counter.

Results are recorded in Table III. Percentages are based on total activity recovered.

TABLE III

Fraction	Deficient Rat Sacrificed After One Hour			Deficient Rat Sacrificed After Three Hours			Normal Rat Sacrificed After One Hour		
	Total Act. μc.	% Total Liver Act.	% Inj. Act.	Total Act. μc.	% Total Liver Act.	% Inj. Act.	Total Act. μc.	% Total Liver Act.	% Inj. Act.
Proteinaceous material	0.196	51.57	1.96	0.097	67.00	0.967	0.250	57.05	2.50
Glycogen	0.012	3.27	0.124	0.015	10.6	0.153	0.052	11.82	0.518
Phospholipid	0.070	18.52	0.703	0.026	17.88	0.258	0.100	22.71	0.995
Fatty acid + non-sap.	0.054	14.10	0.535	0.012	8.04	0.116	0.063	14.33	0.628
Fatty acid	0.038	9.88	0.375	0.006	4.28	0.062	0.038	8.63	0.378
Non-saponifiable	0.012	3.06	0.116	0.005	3.67	0.053	0.031	6.96	0.306
Acid-aqueous	0.060	15.74	0.598	0.010	7.06	0.102	0.026	5.89	0.258
Total	0.380	.	3.80	0.144		1.44	0.438		4.38

Conclusions. Significantly more acetate is utilized by the liver of a normal than of a pantothenic acid deficient rat.

The fact that a much smaller percentage of the acetate utilized by the deficient rat is found in the glycogen fraction is to be expected since the lack of pantothenic acid impairs the ability of rats to synthesize glycogen.

Studies on Adenine Metabolism

E. L. Bennett and B. Krueckel

Previous studies (Biochimica et Biophysics Acta, In press) have shown that intraperitoneally administered adenine is incorporated extensively and rapidly into the soluble nucleotides and the nucleic acids of C57 mice. The cold 10 percent trichloroacetic acid (TCA) extractable soluble nucleotides have been shown to be primarily 5'-adenylic acid (5-AMP) and its derivatives such as adenosine diphosphate (ADP) and adenosine triphosphate (ATP). The extensive incorporation of adenine-4, 6-C^{14} into the nucleotides and nucleic acids has made it possible to determine the turnover rates of these components in various tissues of C57 mice from the disappearance of carbon-14 in the 5'-adenylic acid pool (cold TCA-soluble compounds hydrolyzed to 5-AMP by treatment with calcium hydroxide) and from the adenine in the nucleic acid.

These studies are now being extended to determine separately the half-life of adenine in desoxynucleic acid (DNA) and pentosenucleic acid (PNA) in the various tissues. The enzymatic analytical determinations of specific activity have not been completed, so it must be emphasized that all data and conclusions are subject to revision. The half-life of the soluble nucleotides (5-AMP pool) based on 3 to 16 day data of the intestines was 3-1/2 days; liver, 5 days; carcass, 15 days; and internal organs, 8-1/2 days. Little adenine-C^{14} is incorporated into the DNA of the liver (at 24 hours, less than one percent of that which has been incorporated into the liver PNA). The stomach incorporated 20 percent as much into the DNA as into the PNA; in the case of the carcass (including bone) the amounts incorporated into the DNA and PNA were equal. The specific activity of the DNA adenine in the carcass is higher at 24 hours than the specific activity of the PNA adenine. The disappearance of total activity (up to 16 days after injection) appears to be as rapid or more rapid from the DNA of the stomach, intestines and carcass than from the PNA of these same tissues, indicating a faster renewal rate for DNA than for PNA in these tissues. On the other hand, the carbon-14 activity appears to disappear slowly from the liver and internal organs of the mouse (organs other than lungs, heart, kidneys, intestines, liver and stomach).

In addition, an investigation is being made of factors which may influence the turnover rates of soluble nucleotides, DNA or PNA. The initial experiment, in which aminopterin was administered from 1 to 16 days after the administration of adenine-4, 6-C^{14} indicated no change in the half-life of mononucleotides, DNA, or PNA from that of the controls. Other experiments are planned to study the effect of other factors, such as tumors and irradiation, on the above turnover rates.

The extensive incorporation of adenine into soluble nucleotides such as 5-AMP indicates that an enzyme system is present which is able to perform a conversion of this type:

Adenine + (Ribose-5-phosphate ?) → 5'-adenylic acid.

Preliminary studies have shown that this reaction can be demonstrated using either mouse or pigeon liver homogenates (0.25M sucrose) in the absence of the nuclear fraction and also in the absence of the microsomal fraction. As yet, the synthesis has not been demonstrated in a system in which both the mitochondrial and cytoplasmic supernatant fractions are not present. Further experiments are in progress to purify the enzyme or enzymes involved and to determine, if possible, the intermediates and necessary co-factors.

Glucose Space in the Dog

G. L. Searle

The initial work on the problem of determining the glucose space ("glucose space" is the volume of those free-glucose containing fluids in the body, the glucose of which is in rapid equilibrium with the blood stream glucose) in the intact conscious dog has been previously reported in connection with oxidation studies in the dog (D. D. Feller, I. L. Chaikoff, E. H. Strisower and G. L. Searle; J. Biol. Chem. 188, 865 (1951)). A continuation of these studies is now in progress.

A necessary datum, the dilution of injected C^{14} glucose at zero time, was obtained in the initial studies by extrapolation of the specific activity-time curve of plasma glucose obtained following a single injection of 10 mg of C^{14}-labeled glucose. Calculations arising from this datum gave results that varied greatly. This led to the conclusion that the extremely rapid utilization of glucose by the animal was of prime consideration in this study. It was reasoned that the oxidation of the highly active injected glucose was taking place before it had mixed thoroughly with endogenous glucose of the body, thus leading in many cases to unpredictably high values for glucose space.

Further studies on the problem of glucose metabolism in the intact animal have centered around the continuous infusion of C^{14}-labeled glucose in amounts not exceeding 0.9 mg in six hours. The infused glucose enters the animal in the vena cava near the entrance of the hepatic vein. We believe that this technique gives the greatest possible accuracy in measuring the dilution of the infused C^{14} glucose. Thus we consider that when we have obtained a steady-state situation in the specific activity-time curve of glucose, the mixing of the continuously infused active glucose and that newly produced by the liver of the animal is proceeding under optimum spatial conditions.

Two measurements each in the normal dog, the diabetic dog, and the diabetic dog controlled with insulin, have yielded consistent values in the range of 30 percent of the animal's volume. The latest measurement, carried out on a supposedly normal dog, has brought an exception to the figure stated above, yielding a value of 45 percent of the animal's volume. This anomolous value is currently under investigation via repeated measurements in normal dogs of sufficient number to yield a qualified statistical base line. The animal in which the high value was obtained may, if the need arises, be biopsied to determine suspected Islet malfunction.

Sulfur-containing Components of Photosynthetic Organisms

A. A. Benson

In an investigation of the presence of thioctic acid (6, 8-dithio-octanoic acid) in photosynthetic organisms it is also important to know what other sulfur compounds are involved in plant metabolism. Aside from a few amino acids and sulfate esters, a relatively small number of sulfur compounds are known in plants.

The algae Scenedesmus and Chlorella pyr. were grown on a small scale in a low-sulfate medium containing 20 mc. $S^{35}O_4^=$ per liter. These algae were killed in the light and in the dark and analyzed by paper chromatography. No significant differences between the compounds' dark- and light-killed cells were observed. Ethanol extraction removed 80-85 percent of the activity from the cells. The insoluble residue was hydrolyzed in acid and both it and the alcohol extracts were chromatographed. The fresh alcohol extract had only one major compound. The acid hydrolysate had the expected amino acids, inorganic sulfate and a major product with an R_F slightly less than that of alanine.

The major alcohol-soluble product (10 percent of total algal sulfur) had an R_F similar to leucine and is suspected to be similar to thioctic acid in solubility properties. It is a weak acid although its sodium salt is somewhat soluble in chloroform. Its distribution coefficient between water and chloroform is similar to that reported for 6, 8-dithio-octanoic acid by E. L. Patterson, et al., (J. Am. Chem. Soc., 73, 5919 (1951)). Upon mild Br_2 oxidation the compound slowly changes to a second, somewhat more water-soluble product as indicated by a decrease of about 15 percent in the R_F value. This compound apparently has chemical properties similar to those of the original. Both are converted by brief acid or alkaline hydrolysis at 100° to a compound of much lower R_F (similar to that of nucleotides). Further hydrolysis in acid or by phosphatase gave no change in chromatographic properties.

Very little or no detectable thioctic acid activity in these products has been observed with the Streptococcus faecalis bio-assay. Authentic thioctic acid does not co-chromatograph with this compound. The former is readily detected by a platinic iodide spray test.

Quantitative Assay for Thioctic Acid

R. Clinton Fuller

Because of the probable importance of thioctic acid (6, 8-dithio-octanoic acid) in the mechanism of energy transfer in photosynthesis, it has become desirable to determine the presence of thioctic acid in green plants and to localize quantitatively the site of thioctic acid in its active metabolic state in the cell. Several methods for the determination of thioctic acid have been reported in the literature. However, they are rather time consuming and cumbersome. At the suggestion of Dr. E. L. Patterson of the Lederle

Laboratories a quantitative assay was set up with Streptococcus faecalis (A. T. C. 8083). Our method is an adaptation of that developed at Lederle and it will be published by that group. The quantitative determination is made by measuring the diameter of a zone of growth on bacterial-seeded thioctic-free agar plates. Our growth medium is completely synthetic and is essentially that described by E. E. Snell (J. Biol. Chem., 192, 431 (1951)). A standard dose response curve was determined in each experiment and a sample is shown in Figure 1.

Not only is the assay remarkably sensitive but extremely specific. The following sulfur compounds give no response: thiamin, glutathione, cystine, cysteine, biotin and 5,8-thioctic acid. Both 6,8-thioctic acid and its oxidation product the 6,8-sulfoxide are equally active.

Preliminary experiments indicate that Scenedesmus obliquus contains at least 2.5 γ thioctic acid per gram of dry-weight algae. Of this amount, only 0.2 γ per gram is available to S. faecalis after 80 percent alcohol extraction. The residual 2 γ per gram is made available only after 3 N acid hydrolysis and is equally distributed between the alcohol and the extracted cells. Experiments are in progress to determine chlorophyll and thioctic acid ratio in algae grown under various conditions.

Thioctic acid has been located on two-dimensional paper chromatograms of algal extracts. Generally it seems to run close to the solvent front in phenol and at an R_F of 0.9 in butanol-propionic acid.

To clarify further the active metabolic state of thioctic acid, bioautographic techniques have been developed with the assay organism for the location of active thioctic conjugates on paper chromatograms. It has been demonstrated by the use of this technique that the assay organism will utilize to some extent conjugates of thioctic acid and thiamin and of thioctic acid and cocarboxylase. These conjugates may be important in active thioctic acid metabolism.

Flow System for Kinetic Studies in Photosynthesis

J. A. Bassham

The results of previous kinetic studies of the introduction of C^{14} into the intermediates of carbon fixation during photosynthesis have indicated the importance of obtaining accurate data for the very short exposures of the plant to radiocarbon (0.1 to 10 second). In order to obtain such data, a flow system for introducing C^{14} to the suspension of algae has been devised; this system eliminates certain disadvantages of the batch-wise system previously used. The steady state concentrations of $C^{12}O_2$ can be maintained constant so that the specific activity of the carbon is the only variable changed. In addition, the mixing of the $C^{14}O_2$ of the algae suspension can be made nearly instantaneous.

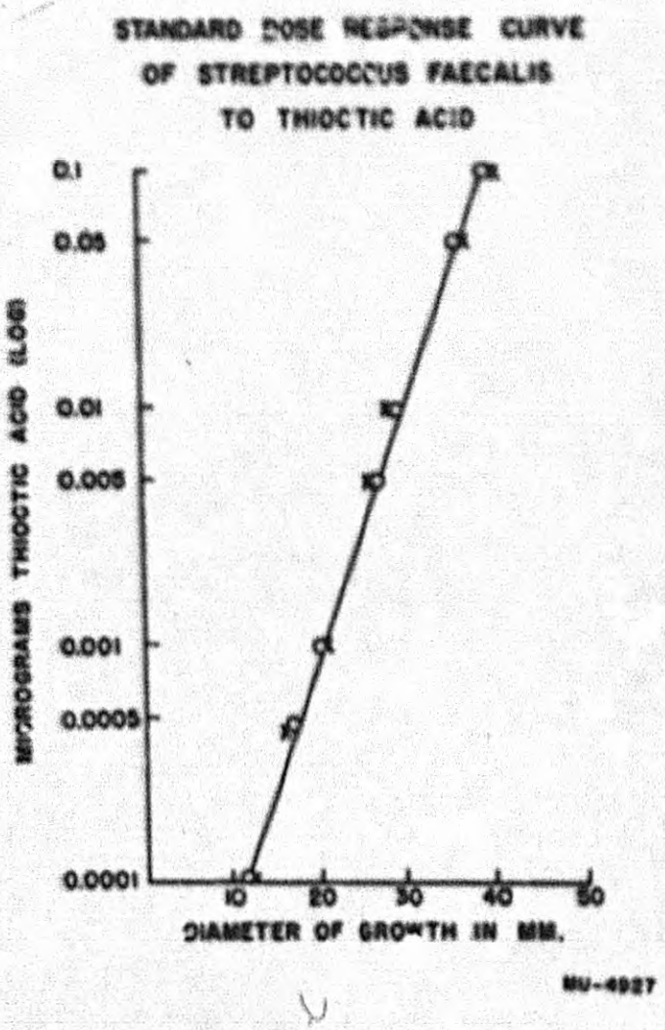

STANDARD DOSE RESPONSE CURVE
OF STREPTOCOCCUS FAECALIS
TO THIOCTIC ACID
MICROGRAMS THIOCTIC ACID (LOG)
0.1
0.05
0.01
0.005
0.001
0.0005
0.0001
10
20
30
40
50
DIAMETER OF GROWTH IN MM.
MU-4927

Fig. 1

The apparatus includes a 250 cc. lucite illumination vessel (4 mm thick) which is illuminated from each side by a bank of fluorescent lights. The suspension of algae in this illumination vessel is continuously aerated with a gas mixture of 4 percent CO_2 in air. A small transparent pump has been designed to take a stream of algae suspension from the bottom of the illumination vessel and force it through several hundred centimeters of transparent plastic tubing (internal diameter of approximately 1 mm illuminated by the same light source as the illumination chamber). The pump develops sufficient pressure to move the suspension through this tubing at a rate of about 18 ml per minute which results in the algae traversing the tube in about 15-20 seconds. A stream of $C^{14}O_2$ dissolved in water at pH 6 is injected into this tubing at various points of known distance from the end of the tubing. A second pump, plus a syringe driven at constant speed, forces this radioactive solution into the algae stream at a constant rate regardless of the point of injection. At the end of the tubing the algae flow into a solution of alcohol which immediately denatures the enzymes. A preliminary experiment has been performed in which the bicarbonate was injected at points 12.0, 7.5, 4.8, and 2.3 seconds, respectively, from the end of the tubing. The rate of fixation was found to be between 40 and 50 million counts per minute per cc of wet-packed algae. The algae suspension used was 0.8 percent by volume wet-packed algae in water. Extracts of these algae are now being analyzed by paper chromatography. With the rates of fixation found in this experiment, it should be possible to obtain, at times as short as 0.2 second, sufficient fixation of C^{14} to permit analysis.

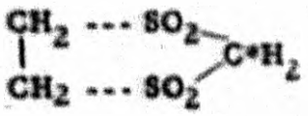
Degradation of Ribulose and Sedoheptulose

Anne Harris and Lorel D. Kay

Ribulose

Attempts to degrade mesoxaldehyde bis-phenylhydrazone, resulting from the periodic acid oxidation of sugar osazones have been continued. The cyclic thioacetal of this aldehyde and 1,2-ethandithiol has been prepared. It was hoped that by thus protecting the carbonyl group, the hydrazone groups could be hydrolyzed. However, in cold concentrated hydrochloric acid the compound did not react. On steam distilling the thioacetal in HCl, it appeared that the acetal was hydrolyzed in preference to the hydrazones. In 50 percent acetaldehyde (another reagent used for hydrolyzing osazones) the thioacetal was recovered unchanged.

Another approach to the degradation of ribulose is the oxidation of the thioacetal to a disulfone, and subsequent hydrolysis, yielding ethylene methylene disulfone,



The labeled methylene would be the C_3 of the original ribulose molecule. This oxidation has been attempted with monoperpthalic acid and perpropionic acid, but in neither case could the expected ethylene methylene disulfone be isolated. Further attempts will be made using different peracids.

An attempt to make the corresponding thioacetal from mesoxaldehyde bisphenylhydrazone and ethyl mercaptan, in hopes that this disulfone would be more easily isolated, has been unsuccessful. The same conditions which were used in preparing the thioacetal from 1, 2-ethandithiol yielded a compound containing no sulfur; this compound was characterized as 1-phenyl, 4-phenylhydrazone pyrazalone-5.

Sedoheptulose

In hopes of determining the amount of activity in carbon No. 1 of sedoheptulose, the reaction of lead tetraacetate on sedoheptulosan was investigated. Two moles of formaldehyde were formed when 30 mg of unlabeled sedoheptulosan were degraded with labeled glucose present to provide radioactive formaldehyde. The method was then used on samples from various experiments with soy beans (Quarterly Report, UCRL-1959, for September, October, November, 1952). The results obtained for the total percentage of activity in C-1 and C-7 are as follows: 5 sec., 4 percent; 5-8 sec., 9 percent; 20 sec., 11 percent; 5 min., 14 percent, 20 days (sample from Oak Ridge), 22 percent. The apparent non-uniform labeling in the long photosynthesis experiments (5 min. - 2 days) may result from an error in the method, although an osazone degradation on the 5 min. sample gave only 6 percent in carbon No. 7.

Another approach to the problem has been an attempt to utilize the dialdehyde resulting from periodate oxidation of sedoheptulosan. It is hoped that if a thioacetal can be formed the ring will then hydrolyze liberating fragments that can be further degraded. Dithioglycol only gave a rubbery polymer. Ethyl mercaptan is now being investigated, using paper chromatography to try to separate reaction products of thioacetal formation and succeeding hydrolysis.

Steady-State Reservoir Sizes in Photosynthesis

A. T. Wilson

An apparatus has been built to investigate the effect of CO_2 on the steady-state reservoir sizes in photosynthesizing algae. This will be described in detail in a later report. Preliminary experiments have been carried out, one of which is described briefly here.

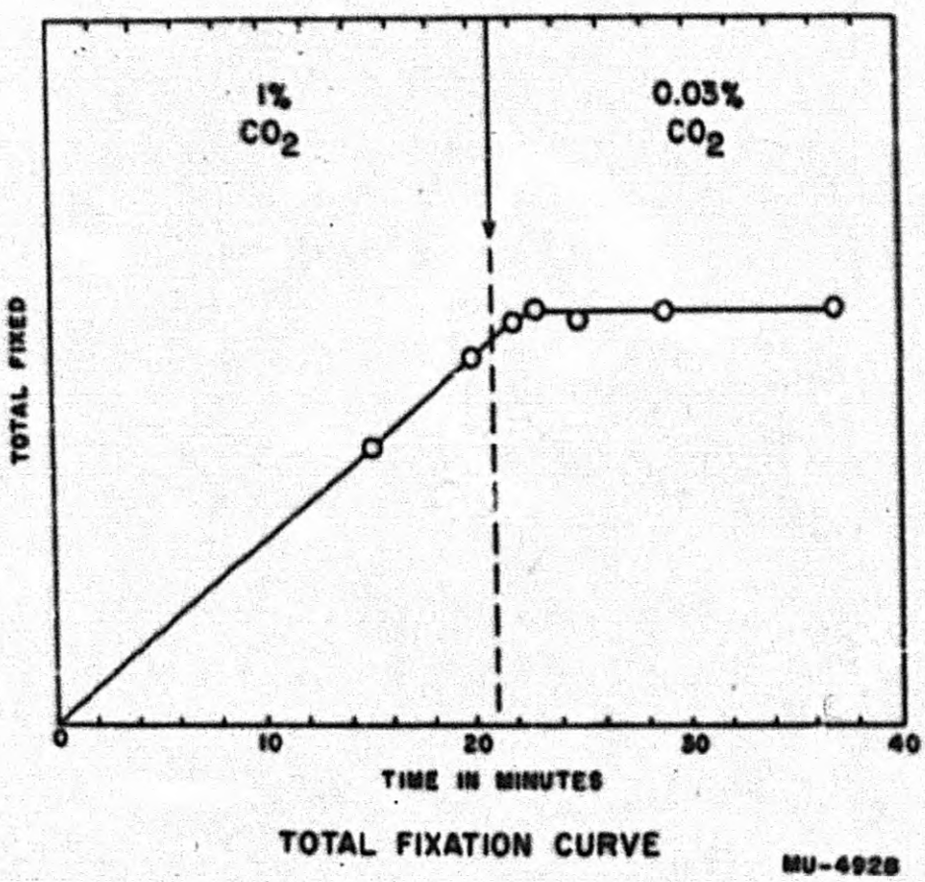
Algae were allowed to photosynthesize in one percent CO_2 (99 percent air) for 35 minutes. At the end of this time the gas stream was changed to one percent $C^{14}O_2$ without altering any other conditions. These conditions

were maintained for 20 minutes when the gas stream was changed to 0.03 percent $C^{14}O_2$ at the same specific activity and at the same rate of flow. During the experiment samples of algae suspension were withdrawn from the illumination vessel and killed in 80 percent alcohol. Aliquot portions were chromatographed on paper and the various reservoir sizes estimated by counting the spots with a Geiger-Müller counter. A plot of the amount fixed is given in Figure 2 and a plot of the reservoir sizes as a function of time as given in Figure 3.

It is of interest to note that the reservoir sizes change profoundly and in a very short time. There seems to be two general kinds of change. First, there is a sudden violent change where the reservoirs of the intermediates fluctuate wildly. Secondly, there is a more gradual overall change of all the intermediates to a lower level; this latter change takes something of the order of 30 minutes before a new steady state is attained.

It is clear even at this early stage that in our conventional photosynthesis experiments we do not have a steady state situation and that during our experiments the ratios of the intermediates are changing very greatly, making the interpretation of all degradation work much more difficult. This may explain why the percentage fixed in short time experiments with phosphoglyceric acid exceeds the theoretical 66-2/3 percent as predicted from our tentative cycle.

Work is proceeding on an experiment where many more points will be taken. If accurate curves can be obtained of the reservoir sizes during the first few minutes after the change, much valuable data could be obtained as to the sequence of the early intermediates.



TOTAL FIXATION CURVE

Fig. 2

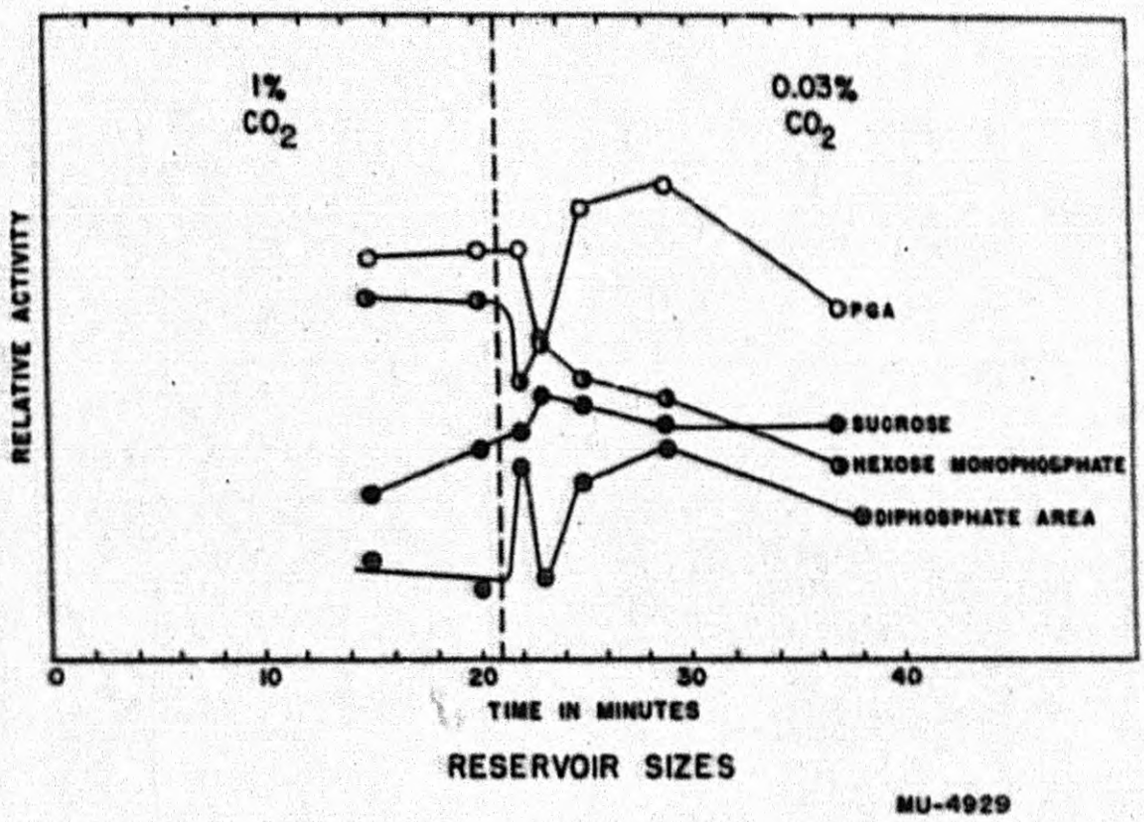

1%
CO_2
0.03%
CO_2
PGA
SUCROSE
HEXOSE MONOPHOSPHATE
DIPHOSPHATE AREA
RELATIVE ACTIVITY
0
10
20
30
40
TIME IN MINUTES
RESERVOIR SIZES
MU-4929

Fig. 3

II. QUARTERLY PROGRESS REPORT. Project 483

W. M. Latimer, Director

A. Metals and High Temperature Thermodynamics

Leo Brewer, LeRoy Bromley, Richard Porter,
Oscar Krikorian and James Kane

Refractory Silicides

Additional heatings of various pairs of metals with silicon to determine the relative stabilities of the metal silicides have been carried out and a summary of all the experiments designed to fix the stabilities of metal silicides is being written.

Molybdenum Chlorides

Work is progressing on the problem of determining the effect of water upon the molecular constituents.

Alkaline Earth Oxide Gases

The spectrum of MgO has been observed in emission as a function of temperature yielding the heat of sublimation to the $^1\Sigma$ state of MgO. Knudsen cell measurements of the total vapor pressure have demonstrated that the $^1\Sigma$ state of MgO cannot account for the total vapor pressure and it therefore is not the ground state as previously believed. A band system believed to arise from triplet states of MgO has been studied and appears to have a lower state which is lower in energy than the $^1\Sigma$ state.

The vapor pressure of fused sodium carbonate is being determined.

Carbon Fluorides

Further experiments are in progress to determine the heat of formation of CF and CF_2 by determination of the emission intensities as a function of temperature.

B. Basic Chemistry, Including Metal Chelates

R. E. Connick, William Jolly, Albin Zielen, Frank Owings,
Howard Mel, Lorin Hepler and John Kury

Studies Involving Liquid Ammonia as a Solvent

The differential method for measuring vapor pressures of liquid ammonia solutions (discussed in the last quarterly report) has been abandoned because of two explosions which occurred when liquid ammonia was confined in glass apparatus at room temperature.

A manometer (with suitable steel containers and connections) has been built for measuring vapor pressures up to 4-1/2 atmospheres with an accuracy of ± 1 mm Hg. The vapor pressures of liquid ammonia solutions of potassium iodide and of silver iodide at 0° C have been measured over wide concentration ranges. These data have been used to calculate relative activity coefficients for the salts, which in turn may be used in estimating the free energy of solution of the salts.

An attempt is being made to use an isopiestic method for determining the vapor pressures of liquid ammonia solutions at room temperature. The vapor pressures of ammonium chloride solutions have been measured and such solutions can serve as reference solutions.

Bromate Thermodynamics

The calorimetric study of the heat of reduction of bromate has been concluded. A series of successful experiments has been performed in which heats were measured for the reduction of bromate by iodide and by bromide. The detailed results and conclusions will soon be submitted for publication in the Journal of the American Chemical Society.

Thermodynamics of Indium

Experiments designed to investigate the equilibria between $In_{(m)}$, In^{+}, In^{+2} and In^{+3} by the method previously described are in progress. Definite indication of the existence of at least one of the lower oxidation state species has been observed. At present we have only enough data to calculate rough values for these equilibrium constants but this lack is being remedied.

The Heat and Entropy of Ionization of Hydrofluoric Acid

The heats of solution of sodium fluoride in water and in aqueous perchloric acid have been measured. These values are used to calculate the heat of ionization of hydrofluoric acid. By combining this heat with the free energy of ionization, we have calculated the entropy of ionization. We found $\Delta H^{o} = -3180$ cal./mole and $\Delta S^{o} = -25.2$ e.u. The detailed data will soon be published in the Journal of the American Chemical Society.

Thermodynamics of Sulfide Ion

This project has been completed and the results will be published shortly in UCRL-2108.

Hydrolytic Polymerization of Zirconium

Work is continuing on the determination of the molar extinction coefficient of the first Zr-TTA (Thenoyltrifluoracetone) complex in 2 M $HClO_4$ solutions.

Potential of the RuO_4^- - RuO_4 Couple

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

Thermodynamics of Thiosulfa.

In the continuation of thiosulfate equilibrium studies, preparation of pure finely divided Ag_2S and Ag has been investigated. For Ag_2S the most satisfactory method is to prepare an Ag_2O precipitate, dissolve in dilute $HClO_4$, pass through purified H_2S, and filter wash, dry and grind the Ag_2S precipitate. In the case of Ag, it has been found nearly impossible to remove final traces of Ag^+ (from treating "reagent" Ag with $HClO_4$ to dissolve Ag_2O impurity). Upon heating the reagent Ag to several hundred degrees Ag_2O slowly decomposes but the Ag metal tends to sinter into hard lumps that cannot conveniently be ground up. To avoid these difficulties one can (1) wash the solution-prepared Ag with cold $Na_2S_2O_3$ (the same type of solutions with which the Ag is to be used) or (2) heat the solid in a very dispersed form as on a large porcelain plate to reduce physical contact of Ag granules, and thus reduce sintering.

Study of Hydrates

Three separate methods of preparation of $CaCl_2 \cdot 2H_2O$ (c) are being pursued. (1) A large sample in a vacuum line is partially hydrated or dehydrated in stages in an effort to arrive at the composition of the stoichiometric compound. Kinetically, over a week is required after the addition or removal of a small amount of water vapor when near this point before equilibrium is again established. (2) "Reagent" chemical (always over-hydrated) is placed in a vacuum dessicator containing H_2SO_4 of appropriate vapor pressure. (3) Wet crystals are obtained by evaporating a solution of $CaCl_2$ at 50° C., the crystals then being placed in vacuum dessicator above. Several weeks are required by methods 2 and 3 to approach stoichiometric composition.

C. Chemical Engineering (Process Chemistry) Section

L. A. Bromley, D. N. Hanson, T. Vermeulen and C. R. Wilke

Preparation of Titanium Metal. A. W. Peterson and L. A. Bromley

Further experiments on the production and purification of TiI_4 were conducted. The purest TiI_4 was made by refluxing the reaction mixture (excess Ti) at low pressure, eliminating contact with the air. Air contact must be eliminated, or oxidation takes place rapidly.

An electrically heated tungsten filament was immersed in the liquid TiI_4. No Ti deposited. It was subsequently discovered that deposition was impossible under the conditions of the above experiment for the following reasons:

(1) No deposition will occur at a TiI_4 v.p. > 40 mm Hg in the Van-Arkel-deBoer process; increasing v.p. over this value even removes previously deposited Ti. (from Runnals and Pidgeon, Journ. Metals 4, 8, p. 843 (1952)).

The result of this is to limit the pressure of operation to < 40 mm Hg and the TiI_4 maximum temperature to 220° C for the above experiment.

(2) It was found that the rate of diffusion of I_2 (rate of removal from hot filament) is a controlling factor in the Van Arkel-deBoer process due to a low equilibrium partial pressure in the reaction

$$TiI_4 \overset{\Delta}{\rightleftharpoons} Ti + 4I$$

(from Runnalls and Pidgeon, Journ. Metals 4, 8, p. 843 (1952)).

The result of this fact is to require fairly pure TiI_4 in order not to reverse the reaction in the vicinity of the hot filament. An experiment should be done to determine the value of the equilibrium partial pressure of I_2.

(3) Film boiling was not attained, due to the difficulty of preventing the wire from burning out. Experiments on the film boiling in water showed that at high heat flux, film boiling suddenly started; the sudden decrease in heat transfer immediately fused the filament. According to Runnalls and Pidgeon, the filament must be at least 1100° C for deposition to occur (film-boiling region).

Thus, a technique must be developed to attain stable film boiling without fusing the filament.

Film Boiling from Sub-cooled Liquids. E. I. Motte and L. A. Bromley

Piping changes have been made so that cold water may be run in the coil of the storage tank so that the liquids to be run may be sub-cooled. The pressure tape to the orifice below the storage tank has been connected to open end manometer tubes so that the pressure difference across the orifice is now read as height of flowing fluid. The cromel vs. alumel thermocouple that measures the amount of sub-cooling of the fluid has been calibrated and installed in the apparatus. The one- and the three-inch orifices have been calibrated by means of a pitot tube assembly in place of the heater element above the nozzle. The calibration of the three-inch orifice was checked by using the ASME orifice discharge coefficients for vena-contracta taps. A five percent variation in the flow rate was found due to the viscous dampening of the fluid in the manometer leg connected at the vena contracta of the orifice. Viscous dampening was used because fluctuations of five to seven centimeters were observed at flow rates around thirteen feet per second. Calibration curves for the two orifices have been prepared. Numerous repairs have been made in the equipment.

Four liquids will be run: ethyl alcohol, carbon tetrachloride, benzene and hexane. The velocity of the liquids will be varied between zero and fifteen feet per second for each of the three sizes of graphite heating elements which will be used. The effect of sub-cooling will be investigated within the limits of the apparatus. The effect of turbulence on heat transfer in forced convection film boiling will also be investigated for one of the liquids.

Thermal Conductivity of Gases at High Temperatures. A. J. Rothman and L. A. Bromley

The furnace windings have been modified and the repaired furnace is now operative. The vacuum piping has been completed and vacuum tested. Measuring circuits are almost complete. The thermal conductivity cell itself has given considerable trouble during construction, due to the fine welds required. At this point almost all major components are assembled and ready for a trial test, except the high-temperature platinum resistance thermometer sealed in quartz, which has also presented construction problems.

Capacity of Perforated Plate Liquid-Vapor Contacting Columns. C. D. Hunt and D. N. Hanson

Data on liquid properties indicate no significant effect of liquid viscosity on pressure drop; however, there is a definite effect of liquid-solid wetting properties, distinct from gas-liquid interfacial tension.

Data are now being taken to determine the effect in the pressure drop vs. gas flow of gas-liquid interfacial tension and liquid density.

The column has been modified to include a second perforated plate 20 inches above the existing plate to study entrainment.

Mass Transfer in Agitated Liquid Systems. L. Fick, H. Rea and T. Vermeulen

A general study of mixing in closed cylindrical vessels has been continued. In comparisons of unbaffled and baffled tanks, 50 percent higher speed was found necessary to produce the same interfacial area in an unbaffled tank; this corresponds to a slight decrease in power consumed per unit of area produced.

The peripheral speed of the impeller has been identified to control the interfacial area, independently of impeller width. As the power required is directly proportional to the width, the width should be reduced to a value just sufficient for complete mixing. Experiments are now in progress to measure the uniformity of mixtures under varying conditions of agitation, to find the lowest practicable impeller widths.

Previous studies had indicated that the interfacial area is insensitive to viscosity variations. Because this result disagrees with the theoretical analyses of droplet breakup, the interfacial-area behavior of mineral oil/water mixtures is being investigated in detail.

Preliminary measurements of mass-transfer rates in liquid-liquid mixtures have shown that equilibrium is approached within seconds, so rapidly that accurate measurements of rate are not possible in the present apparatus. This result indicates that nearly all heterogeneous reactions in which the rate increases with stirring speed will involve a reaction at the interface as the rate-determining step.

Gas-Phase Mass Transfer Studies. E. J. Lynch and C. R. Wilke

The unit for studying rates of evaporation from porous pellets in packed beds has been designed and partially assembled, pending completion of parts by the Radiation Laboratory shops.

The apparatus for measuring vapor diffusion coefficients is being repaired and moved to an area adjacent to the drying unit.

Psychrometric studies are in progress to test the validity of use of the film pressure factor in convective mass transfer. The results thus far are not conclusive since considerable difficulty has been experienced in obtaining satisfactory gas samples and in maintaining a suitable degree of wetness of the wick. Efforts are being made to overcome these difficulties.

Thermal Diffusion in Liquids. J. Powers and C. R. Wilke

Moderate revisions were made on the Liquid Thermal Diffusion apparatus and a series of three runs were made to investigate the effect of flow rate on the separation of ethyl-alcohol from water. The flow rate has no effect on the separation over the range from 0.06 to 0.6 cm/minute in the apparatus. Further changes are being made in order to investigate higher flow rates.