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CHEMISTRY DIVISION QUARTERLY REPORT

March, April, May, 1953

June 25, 1953

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NUCLEAR CHEMISTRY

G. T. Seaborg and I. Perlman

RARE EARTH ISOTOPES

Maynard Michel and Walter Nervik

During the last quarter, the time-of-flight mass spectrometer has been used to collect samples of the isotopes of ytterbium, thulium, and erbium formed by high-energy spallation of tantalum. As reported previously, a preliminary survey with a Nier type mass spectrometer was made in order to make tentative assignments of mass numbers to the isotopes observed. The results reported here are final assignments on all the isotopes of the above three elements formed in high yield in this reaction.

Ytterbium

On the basis of several runs with chemically separated ytterbium, samples of the ytterbium isotopes have been collected to establish the mass numbers for the various decay periods observed. The simplicity of geometry of the time-of-flight machine has made it possible for small amounts of neutral vaporized source material to be collected on the sample plates. For this reason, no more than three isotopes are collected during any one run, the fourth available collection plate being used to monitor the vaporized neutral material. With the elements being studied, which are among the least efficient thermal ionizers in the rare earth region, the amount of vaporized material is quite high. However, by suitable design of the collection system this contamination has been reduced considerably, and indications are that the scattered neutral atoms can eventually be eliminated.

Collections of ytterbium have yielded the following isotopes:

Isotope	Half-life
Yb^{166}	58 ± 1 hours (plus 7.7 hour growth of Tm^{166})
Yb^{169}	31 days

No isotope of mass 165 or 167 was seen, although chemical separations indicate that a short-lived (70 min.) isotope of ytterbium observed in the gross decay is the parent of Tm^{167} which has been directly assigned.

Lutetium

Repeated attempts have failed to effect the separation of the neutron-deficient isotopes of lutetium on the ion separator, although ionization efficiency measurements indicate that this element should be fairly easily ionized. Decay of the gross pure lutetium fraction of the January 23 bombardment, however, indicates the presence of a large amount of a 33-day activity. There are no reported lutetium isotopes with half-lives of this order of magnitude. Yb^{169}, however, has a half-life of 32 days and may be the daughter of Lu^{169}, although this nuclide has not been previously reported.

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Thulium

Three thulium isotopes were collected as summarized below:

Isotope	Half-life	Decay Characteristics
Tm^{165}	29 ± 1 hours	EC; 227, 282 kev γ (in Tm^{165}-Er^{165} equilibrium mixture)
Tm^{166}	8 hours	EC; 180, 225 kev γ
Tm^{167}	9.5 days	EC; 115, 202, 515, 720 kev γ

The isotope of mass 165 has not been reported previously. Several samples have been followed for decay, the largest being about 2000 counts per minute on a Geiger counter. The samples were more than sufficient for determination of the gamma ray spectrum on a sodium iodide scintillation spectrometer.

Erbium

The erbium isotopes collected are listed below:

Isotope	Half-life
Er^{160}	30 ± 1 hours
Er^{161}	3.5 hours

No significant amount of activity was observed at mass 165 when the sample was run soon after bombardment. However, a 10-hour period has been observed as the decay product of Tm^{165} in agreement with the previous assignment of Er^{165}.

In addition to Er^{160} and Er^{161}, a small amount of Er^{163} has been isolated on the ion separator. Here again the activity level was too low to make definite assignments of half-life and decay characteristics. The sample does show an initial decay half-life of several hours followed by a tail which has a half-life of the order of days. More significant information on the Er^{163} may be obtained from an experiment in which erbium was separated from the gross rare earths 3 days after bombardment. Presumably at this time the only erbium activities which should have been present in significant amount are 29-hour Er^{160}, 10-hour Er^{165} (daughter of 29-hour Tm^{165}), and Er^{165} if it has a half-life longer than 6 hours. The decay of this gross erbium fraction shows the presence of at least three activities. First, a growth of approximately 4-hour half-life, then an initial decay of 29 hours, and finally, a long-lived tail of approximately 14.5 days. Assignment of the 4-hour and 14.5-day activities will have to be delayed until an experiment is completed in which holmium is milked from the 14.5-day activity.

THALLIUM ISOTOPES

Maynard Michel

Recently the neutron-deficient thallium isotopes formed in the bombardment of gold by helium ions have been assigned directly on the time-of-flight spectrometer. Previous assignment had been attempted and will be summarized also.

The bombardment of gold with 40-Mev helium ions yields three resolvable periods of 27-, 7-, and 1.8-hour half-life. These have been assigned to Tl^{200}, Tl^{199}, and Tl^{198} respectively.[1] A previous separation of these isotopes in the time-of-flight mass spectrometer resulted in yields for only mass 199 and mass 198. The mass 199 sample decayed with a 7.2-hour half-life in fair agreement with the resolved 7-hour period. However, the mass 198 sample had two periods associated with it of about 1.5 and 5.2 hours. Only recently this result has been verified by collecting much larger samples and carefully following the decay. In addition, the gamma-ray spectrum of each separated sample was observed. The separation was made a day after bombardment, so that no 1.8-hour thallium would be present. The results are given below:

Isotope	Half-life	Initial Activity
Tl^{198}	5.30 ± 0.2 hours	2500 c/m
Tl^{199}	7.4 ± 0.1 hours	13,000 c/m
Tl^{200}	28 hours	1000 c/m

The gamma rays previously reported for Tl^{199} and Tl^{200} were verified[2] and the gamma ray analysis of the new isomer showed only two transitions, at 405 kev and 610 kev. The decay of the mass 200 sample showed two periods, one being the 28-hour isotope previously assigned to this mass and a second being about 8 hours. One would expect a small amount of Tl^{199} to be collected on the mass 200 plate because of the small amount of overlap in the separator and the large amount of Tl^{199} present. However the amount collected is about two or three times the amount expected from previous experience with the instrument. This is not conclusive proof, but an experiment is planned to verify or eliminate this possible isomer.

References

1. D. A. Orth, L. Marquez, W. J. Heiman, and D. H. Templeton, Phys. Rev. 75, 1100 (1949).

2. H. I. Israel and R. G. Wilkinson, Phys. Rev. 83, 1051 (1951).

PHOTON SPECTRUM FROM DECAY OF Am^{241}

Harold Jaffe and I. Perlman

The following x-ray lines from the decay of Am^{241} were observed with a bent crystal spectrometer.

Line	Energy	Energy (Extrapolated)	Intensity
$NpL_{\gamma} - L_{\gamma_4}$	22.19 ± 0.04	22.16 - 22.22	3
NpL_{γ_6}	21.51 ± 0.04	21.49	10
NpL_{γ_3}	21.31 ± 0.04	21.34	7
NpL_{γ_2}	21.12 ± 0.04	21.09	8
NpL_{γ_1}	20.82 ± 0.02	20.77	34
NpL_{γ_5}	20.15 ± 0.08	20.09	2
AmL_{β_1}	18.76 ± 0.04	18.80	6
NpL_{β_3}	18.02 ± 0.02	17.98	13
NpL_{β_1}	17.78 ± 0.01	17.74	100
NpL_{β_5}	17.58 ± 0.06	17.51	3
NpL_{β_4}	17.10 ± 0.02	17.06	16
NpL_{β_2}	16.89 ± 0.02	16.84	13
NpL_{β_6}	16.15 ± 0.06	16.11	1
NpL_{η}	15.90 ± 0.03	15.85	2
AmL_{α_1}	14.66 ± 0.03	14.61	10
NpL_{α_1}	13.98 ± 0.03	13.94	64
NpL_{α_2}	13.80 ± 0.03	13.76	8

The americium lines (AmL_{β_1} and AmL_{α_1}) are probably due to fluorescent excitation by the abundant "60" Kev gamma.

Gamma Rays

Energy	Intensity (relative to NpL_{β_1})
59.65 ± 0.13	350
59.62 ± 0.06 (second order)	
26.38 ± 0.04	35

The relative intensities of the x-rays from a given L level are as follows:

L_I $L_{\beta_4} : L_{\beta_3} : L_{\gamma_2} : L_{\gamma_3} : L_{\gamma_4} - L_{\gamma_{4'}} = 100 : 81 : 47 : 40 : 17$

L_{II} $L_{\beta_1} : L_{\gamma_1} : L_{\gamma_6} : L\eta : L_{\gamma_5} = 100 : 34 : 10 : 2.3 : 1.9$

L_{III} $L_{\alpha_1} : L_{\beta_2} : L_{\alpha_2} : L_{\beta_5} : L_{\beta_6} = 100 : 20 : 12 : 5 : 2$

Analysis of the x-ray intensities in conjunction with the decay scheme of Asaro, et al.,[1] and Kinsey's fluorescent yields gives the following L shell conversion coefficients for the 60-Kev gamma.

$\alpha_{L_I} = 0.7$

$\alpha_{L_{II}} = 0.6$

$\alpha_{L_{III}} = 0.3$

$\alpha_L = 1.6$

This is consistent with an assignment of electric dipole radiation to the transition.

1 F. Asaro, F. L. Reynolds, and I. Perlman, Phys. Rev. 87, 227 (1952).

RELATIVE YIELDS OF Co^{58} AND Co^{58m} ISOMERS FROM THE (α, n) REACTION ON MANGANESE

Harris Levy

In studying the fission of bismuth by high-energy protons, William Biller[1] had occasion to measure the yields of several nuclides that had isomeric states. In all cases where it was possible to determine or estimate the primary yields, the formation of the isomer with the greater spin, whether it was the ground state or the excited state, was favored over that of the state with the lower spin, often to the apparent exclusion of the latter. Because of this consistent favoring of the higher spin state of isomer pairs in the high-energy fission of bismuth, it was felt of interest to investigate further the formation of isomer pairs in nuclear reactions in general.

High-energy fission and spallation are rather complex processes. Rather, it seemed desirable to investigate the formation of isomers by the simplest type of nuclear reaction, X(a, b)Y, where Y can be found in either its ground state or in a metastable excited state after the reaction has been completed.

In such a reaction, upon emission of particle b from the compound nucleus, the residual nucleus is generally left in a highly excited state. This highly excited state of Y (usually written Y*) then decays by successive gamma-ray emission to either the ground state or the metastable isomer. It has been suggested by some[2,3] that if the highly excited Y* is formed in a number of states covering a wide range of spin values, then all other effects should be washed out, and the relative number of nuclei ending up in each of the two isomeric states will be determined simply by their respective statistical weights, 2I + 1 (where I is the spin of the state in question). In other words, we might write:

$$\frac{\sigma_m}{\sigma_g} = \frac{2I_m + 1}{2I_g + 1}$$

where σ_m and I_m are the cross section and the spin for the metastable state, and σ_g and I_g are the corresponding terms for the ground state.

In the reaction X(a, b)Y* as one increases the energy of the bombarding particle, a, reaction channels involving larger ℓ values become increasingly important. (Here ℓ is the angular momentum which a brings into the reaction.) As ℓ values increase, the excited residual nucleus, Y*, covers a wider and wider range of spin values. Therefore, if this statistical determination is valid, one would expect that as the energy of a is increased, the ratio $\sigma m/\sigma g$ would approach a limiting value of $(2I_m + 1)/(2I_g + 1)$.

The formation of Co^{58} isomers from the Mn^{55} (α, n) reaction was chosen for study. This reaction has several advantages, an important one being that it is possible to observe the activity of the ground state Co^{58} to the exclusion of Co^{58m} and Co^{57}. Since Co^{58m} decays 100 percent by isomeric transition, one can observe the growth and decay of Co^{58}. By analyzing the growth and decay of the activity curve for the Co^{58} activity, one can obtain the relative initial amounts of Co^{58} and Co^{58m} without resort to the frequently tricky business of estimating counting efficiencies. As the work progressed, it was found possible to go up to alpha particle energies sufficient to bring

$\sigma m/\sigma g$ up to the value of $(2I_m + 1)/(2I_g + 1)$ without getting any cobalt activities that interfered with the observation of the Co^{58} activity.

At low energies, below the (α, 2n) threshold, the cobalt activity was followed on a Geiger counter with sufficient aluminum absorber to block out all radiations from Co^{58m}. Thus, the growth and decay of the ground state Co^{58} alone was observed. At higher energies where Co^{57} was also formed, the cobalt activity was counted on a sodium iodide scintillation counter where it was possible to follow the Co^{58} by means of the characteristic 810-Kev gamma ray which appears in its decay.

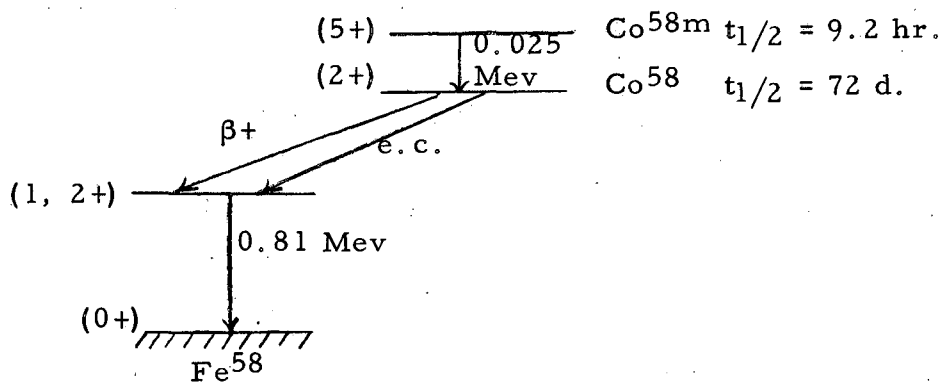

Fig. 1

Decay schemes[4] of Co^{58m} and Co^{58}

$$\frac{2I_m + 1}{2I_g + 1} = \frac{11}{5} = 2.2$$

The results of bombardments at various alpha energies are listed below, including one result obtained by K. Strauch[3] at 17 Mev.

Table I

Ratio of Cross Sections for Co^{58m} and Co^{58} from Mn(α, n)

Incident α-particle energy	$\sigma m/\sigma g$
9.5	0.97
~ 11.3	1.2
14.4	1.4
17	1.7[3]
18.4	2.2
20.9	3.6

The target material was powdered $MnSO_4 \cdot H_2O$. The targets were thick enough so that the alpha particles were considerably degraded in energy while traversing the thickness of the target. The values of σ_m/σ_g given in the table therefore represent some sort of mean value over the energy range that the alpha particles would have in the target material. The alpha energies listed are those which the alpha particles possess upon first striking the target.

It is seen from Table I that as the alpha-particle energy is increased, σ_m/σ_g steadily increases. At an incident alpha energy of 18.4 Mev, $\sigma m/\sigma g$ has reached the value of $(2I_m + 1)/(2I_g + 1) = 2.2$, and at energies of ~20 Mev the ratio σ_m/σ_g continues to increase beyond this value that we had throught might prove to be a limiting value.

The fact that the ratio $(2I_m + 1)/(2I_g + 1)$ does not impose a limiting value on σ_m/σ_g is not surprising if one takes the following approach to the situation. It is known from the study of (n, γ) reactions that excited nuclei, even in fairly high energy states, de-excite themselves by emission of a relatively few gamma rays (about two or three). It also appears that these gamma rays are of a low multipole order (dipole and/or quadrupole). Therefore, there is only a small spin change upon emission of each of these gamma rays. Also, if all other factors are equal, the transition to competing states will favor those of higher spin because of their greater statistical weight. Thus, if we had more than one possible final state for the nucleus Y, we would expect it to end up mainly in a state whose spin was not far away from that of Y*, with the statistical factor helping to increase the number ending in the higher spin state.

As mentioned before, as we increase the bombarding energy, we bring in larger and larger ℓ values. This means that we get an increasing probability that Y* is formed in a high spin state. This fact coupled with the reasoning in the previous paragraph would lead us to the following conclusion: As one increases the bombarding energy, one merely increases the probability of forming the isomer with the higher spin. There would be no reason to expect any special limiting value for the ratio $\sigma m/\sigma g$.

References

1. William Biller, Ph. D. thesis, University of California Radiation Laboratory Classified Report UCRL-2067 (1953).

2. E. Segrè and A. C. Helmholz, Rev. Modern Phys. 21, 271 (1949).

3. K. Strauch, Phys. Rev. 79, 487 (1950).

4. J. M. Hollander, I. Perlman, and G. T. Seaborg, "Table of Isotopes" (rev. ed.) University of California Radiation Laboratory Unclassified Report UCRL-1928 (1952).

PATTERNS IN ALPHA SPECTRA OF EVEN-EVEN NUCLEI

Frank Asaro and I. Perlman

The first rule for even-even alpha emitters is that the most prominent alpha group leads to the ground state of the product nucleus, as would be expected from previous alpha decay theory. (This is not the case for nuclear types having odd nucleons.) In addition, an alpha group is invariably found which leads to a level with spin 2 and even parity and the abundance of this group likewise conforms in first approximation with the expectations from unadorned alpha decay theory. The energy level of this excited state will be termed the first even spin state and lies about 40 kev above the ground state at plutonium, increasing with decreasing mass number as already described.[1,2] In low abundance are found alpha groups leading to other levels which we shall term second and third even spin states. In the few cases for which gamma ray data are available it seems probable that these levels have even parity as well as even spin and may very well be 4+ and 6+ states. There is some fragmentary evidence in our work that an odd spin-odd parity state is appearing in a limited region, but this will not be discussed further at present.

Bohr and Mottelson[3] have suggested that nuclides well beyond a closed shell have states in which the nucleus acts as a rigid rotator. Such rotational levels should be proportional to $J(J+1)$ where J is the total angular momentum quantum number. If we consider the 2+ and 4+ states to be rotational states, the ratio of the energies should be 3.3. Fig. 1 shows experimental ratios for ten nuclei in the heavy element region plotted against neutron number. It is fairly certain that corresponding states are compared here although in only one case, Cm^{242}, have the necessary measurements been made to establish this state as 4+.[4] The heaviest nuclei show remarkably close agreement with the expectations for the postulated rotational states and there appears to be a progressive departure from the ratio 3.3 toward lighter nuclei. (There is no convincing justification for plotting these data strictly with respect to neutron number as is done here; in fact, it is not to be expected that the nuclear deformation which defines these levels is simply a function of the neutron number.)

Gamma ray data have been used to infer the existence of the third even-spin state for three species. The ratios of the third to the first levels are indicated in Fig. 1 in relation to the theoretical value 7 for the third rotational state, $J = 6$.

In the study of the alpha spectra of most of the nuclides shown in Fig. 1, it became clear that the alpha transitions leading to the second even spin states were highly hindered. That is, the measured partial half-lives were much longer than expected simply from the energy and nuclear charge. (It will be remembered that the ground-state transitions and those leading to the first even-spin states are in first approximation unhindered.) The Cm^{242} alpha group leading to the second even-spin state, as an example, has a half-life almost 400-fold longer than expected from theory. On examining this relationship for alpha emitters of lower elements, it was found that as the energy of the second even-spin state increased, the hindrance factor decreased. For the species examined so far, the logarithm of the hindrance factor varies lineraly with the atomic number (Fig. 2). There is no quantitative explanation yet known for the close agreement of this function. (It will be noted that a few points lie off the curve.)

If we assume that the same spin change is involved in each of these transitions, an explanation cannot lie in simple fashion in this direction, both because of the large hindrance factors in some cases and because of the wide variation. A possible explanation lies in the assumption of a progressive change in asymmetry of charge on leaving the closed shells in the vicinity of lead. The potential barrier will then be spherically nonsymmetrical and if the alpha particles of a type have a preferred direction of emission, any progressive change in charge distribution will be reflected in a progressive change in the ease with which the alpha particle can leave.

References

1. F. Asaro and I. Perlman, Phys. Rev. 87, 393 (1952).

2. S. Rosenblum and M. Valadares, Comt. Rend. 235, 711 (1952).

3. A. Bohr and B. Mottelson, Phys. Rev. 89, 316 (1953).

4. F. Asaro, S. G. Thompson, and I. Perlman, "The Alpha Spectra of Cm^{242}, Cm^{243}, and Cm^{244}," Phys. Rev., submitted for publication.

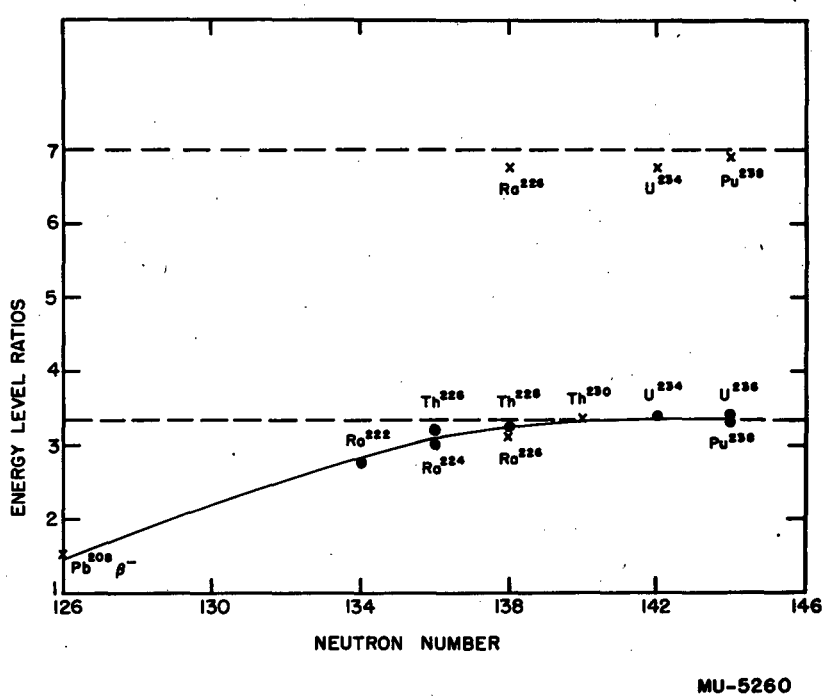
ENERGY LEVEL RATIOS
NEUTRON NUMBER
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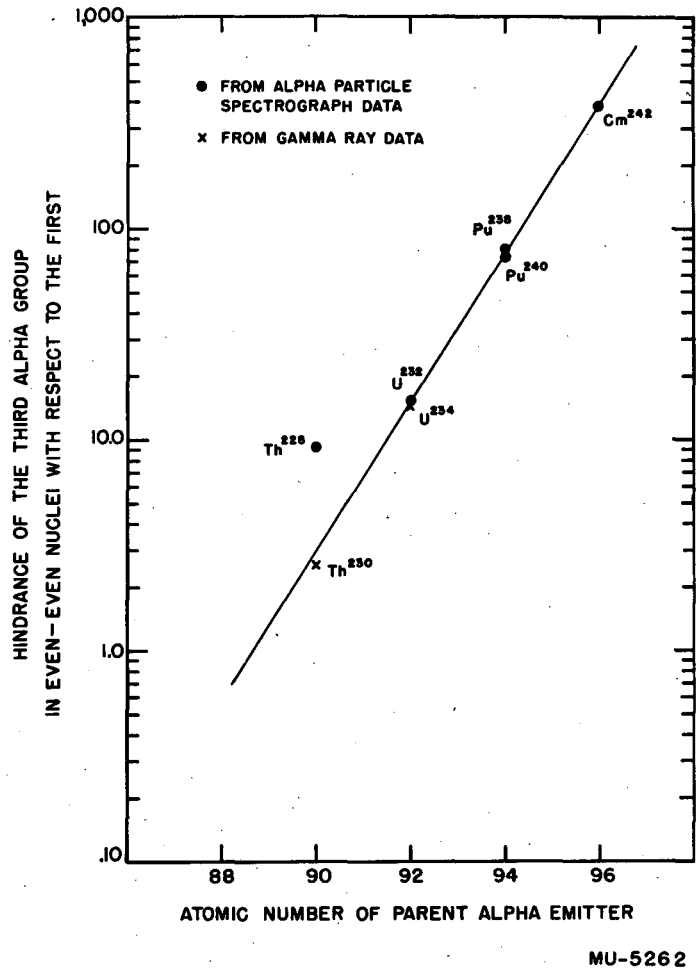
Fig. 1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● FROM ALPHA PARTICLE SPECTROGRAPH DATA
× FROM GAMMA RAY DATA
Cm242
Pu238
Pu240
U232
U234
Th228
Th230
HINDRANCE OF THE THIRD ALPHA GROUP
IN EVEN-EVEN NUCLEI WITH RESPECT TO THE FIRST
ATOMIC NUMBER OF PARENT ALPHA EMITTER
MU-5262

Fig. 2

IRRADIATION OF CERIC SULFATE AND FORMIC ACID

Harry E. Spencer

Ceric sulfate and formic acid in dilute sulfuric acid solution have been irradiated with x-rays from a full wave rectified Machlett AEG 50 T tube operated at 50 PKV and 45 milliamperes. The x-rays were filtered by 1/32 inch of pyrex glass, and the temperature was maintained at 27 ± 0.5° C. The volume of solution was 100 cc. with a gas space above the solution of about 115 cc. All solutions were degassed before irradiation.

The number of cerous ions and molecules of carbon dioxide produced are concentration dependent.

Work continues on this reaction.

Irradiation Number	Hours of Irradiation	H_2SO_4 moles/L.	Ce^{+4} moles/L.	HCOOH moles/L.	Moles x 10^4 Total Gas	H_2	O_2	CO_2
C	0	1.45	0.00942	0.0094	--	--	--	--
C-4	20	1.45	0.00495	0.0083	2.67	0.649	0.880	1.16
C-3	20	1.45	0.00499	0.0081	2.66	0.633	0.876	1.15
C-2	23	1.45	0.0042	0.0082	--	--	--	--
C-1	22	1.45	0.0043	--	3.01	0.78	0.93	1.26
D	0	1.4	0.00627	0.0048	--	--	--	--
D-4	5	1.4	0.00523	0.0045	0.64	0.172	0.214	0.245
D-3	10	1.4	0.00437	0.0044	1.20	0.321	0.432	0.450
D-2	15	1.4	0.00350	0.0042	1.64	0.466	0.607	0.572
D-1	20	1.4	0.00253	0.0040	2.27	0.663	0.858	0.735

FURNACE SPECTRA OF PLUTONIUM

John G. Conway

The work on the furnace spectra of plutonium has been completed and will appear shortly as report UCRL-2213.

ZEEMAN MAGNET

John G. Conway

The Zeeman magnet has been delivered and installed. Following the adjustment of the power supply and calibration of the field it will be ready for spectrographic work.

RULING FINE LINES ON QUARTZ

Herman P. Robinson

A simple method has been developed to rule fine lines on fused quartz. If an attempt is made to rule the surface of fused quartz with a diamond, it is found that the edges of the lines tend to chip or otherwise give an uneven ruled mark. Ordinary glass is free from this difficulty and this suggested the possibility of treating the quartz to give the surface the properties of a soft glass, and then rule on this treated surface.

The method is as follows: A layer of lead is first vacuum-evaporated onto the quartz surface. The quantity is not critical, but ten or twenty mircograms per square centimeter is a satisfactory thickness. The quartz is then heated in air to a dull red heat. The lead first oxidizes and then reacts with the quartz surface to form a lead glass. This surface can be ruled easily with a diamond splinter with no chipping of the lines whatever.

After the ruling is completed the surface may be hardened by vacuum-evaporating a layer of silicon monoxide over the lead and again heating to a dull red heat. The monoxide oxidizes to silicon doixide with the apparent hardness of the original fused quartz.

This work was done in order to prepare some transparent fused quartz length standards which could be certified by the Bureau of Standards.

VAPOR-PRESSURE MEASUREMENTS

Stephen C. Carniglia

The horizontal twin effusion apparatus for making comparative vapor-pressure measurements in the heavy element region has been readied. Calibration of the thermocouple by means of the observed melting of standard metal samples has been completed. Control experiments have demonstrated satisfactory behavior as regards collimation, condensation, and freedom from scattering of the effusant.

Absolute vapor-pressure measurements made on plutonium trifluoride (with only one side of the apparatus in use) confirm the results of Phipps, Sears, Seifert, and Simpson[1] well within the stated uncertainty of their data; although our measurements, being for control purposes only, were made over a quite limited temperature range: 940° - 1170° C.

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1 T. E. Phipps, G. W. Sears, R. L. Seifert, and O. C. Simpson, J. Chem. Phys. 18, 713 (1950).

BIO-ORGANIC CHEMISTRY

M. Calvin and A. A. Benson

THE ROLE OF THIOCTIC ACID IN THE HILL REACTION

D. F. Bradley and M. Calvin

It has recently been proposed[1] that the primary conversion of electromagnetic energy to chemical bond energy in photosynthesis is mediated by 6-thioctic acid (6,8-dithiooctanoic acid, 6 T).* Because of the strain in its five-membered ring, this molecule provides a chemical bond that may be broken by a ca. 30 kcal/mole quantum transferred to it from the excited state of chlorophyll. The resulting diradical then abstracts from hydrogen from a donor derived from water, forming a dithiol, 6 DT, and a moiety whose oxidizing power is ultimately the source of molecular oxygen. The dithiol may subsequently transfer its hydrogen to a suitable acceptor such as DPN[2] or FAD, distributing the reducing power and regenerating the cyclic disulfide, 6 T. Energy of the quantum is conserved in this process provided that the reduction potential of the hydrogen acceptor exceeds that of the original donor. From established thermodynamic considerations, at least four of these 6 T "cycles" must occur for the net reduction to carbohydrate of a molecule of carbon dioxide, and it is therefore probable that subsequent reactions in the sequence would involve reoxidation of the reducing hydrogen and storage of the energy in some chemical form such as high energy phosphate.[2,3,4]

If 6 T is operating in the manner described, it should be possible to realize conditions under which synthetic 6 T added to the plant could be utilized to stimulate the quantum conversion, resulting in a net higher rate of photosynthesis. The demonstration of such a stimulation in the Hill reaction, in which the photochemical apparatus is experimentally separated from the carbon dioxide reduction system, would provide even more satisfactory confirmatory evidence for the proposed mechanism of quantum conversion.

This paper reports a stimulation of the Hill reaction by 6 T in cellular chloroplast preparations[5] of the unicellular algae Scenedesmus under conditions which are highly specific with respect to 6 T, the organism involved, and the physical conditions of the experiment. These conditions are completely consistent with what would be expected from the theory described above.

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*The following abbreviations will be used throughout this paper:

6 T - 6,8-dithiooctanoic acid
6 DT - 6,8-dithioloctanoic acid
6 MD - 6,8-dithiooctanoic acid monoxide
6 TR - 6,8-dithiyloctanoic acid
5 T - 5,8-dithiooctanoic acid
4 T - 4,8-dithiooctanoic acid
DPN - diphosphopyridine nucleotide
FAD - flavin adenine dinucleotide

Materials and Methods

Scenedsemus obliquus, Chlorella pyrenoidosa and Synechococcus cedorum were grown in continuous culture under conditions that have been described previously,[6,7] and were harvested daily. The algae were centrifuged (1900 x g) and washed with distilled water four times, and resuspended in M/15 K-phosphate + M/100 KCl buffer (pH = 6.7)[8,9] to the desired suspension density, generally 20 mm^3 wet packed cells/ml. The pH of the resulting suspension was identical with that of the original buffer. Scenedesmus which were stored at 6° C in the dark for 48 hours suffered no loss in the rate of quinone-dependent, photochemical oxygen production.

Quinone was purified by sublimation (m.p. = 113-115°) and stored at -10° C in the dark. Solutions of 1-12 mg/ml in distilled water were stored in red glass vessels in the dark and used within four hours after preparation. Solutions of dl-6 T (cryst.), dl-5 T (cryst.), dl-4 T (cryst.), 6 DT (oil), and 6 MD (oil) were prepared in M/3 phosphate buffer (pH = 6.7) in concentrations of 0.25-1.0 mg/0.05 ml.

Standard double side-arm Warburg flasks were used. All reactions were carried out at 15.7° C. The light field was supplied by seven General Electric photospots and was homogenized by passing the beams through a water-cooled layer of 2-1/2-mm glass beads. The resulting field (26,000 lux) varied by less than four percent throughout the entire thermostat.

Light screens were made from brass screening which was wrapped around the vessels. The screens were calibrated against both a Cary Recording Spectrophotometer and a General Electric Photovoltaic cell for relative transmission. There was no selective transmission and the results of the two methods agreed within two percent.

Chlorophyll content was determined by centrifuging aliquots of the suspension and extracting the centrifugate with aqueous ethanol. The visible absorption spectrum of the extract was determined on a Cary Spectrophotometer, and the concentration of chlorophyll (chl a) calculated from the transmission at the 662 mμ absorption maxima (ϵ_{max} assumed 9×10^4 liter $mole^{-1}$ cm^{-1}), mean deviation of duplicate runs being 1.1 percent.[10]

The standard pattern for the experiments was as follows: 2.0 ml of the algal suspension was transferred to each manometer flask, which contained 0.2 ml of 20 percent KOH and a pleated filter strip in the center well. The vessels were then allowed to stand aerobically in the dark for one hour, at which time 0.5 ml of quinone solution was added to a side arm of each vessel, 0.05 ml 6 T solution to each experimental sample of algae, and 0.05 ml M/3 phosphate buffer to each control algae sample. The vessels were then shaken for ten minutes aerobically in the dark, followed by 10 minutes of flushing with commercial N_2. Ten minutes later, when pressure equilibrium had been established, the quinone solutions were tipped into the algae, and after fifteen minutes of anaerobic dark reaction the lights were turned on.[8]

Experimental

Illuminated Scenedesmus cells consistently produced photochemical oxygen with quinone as oxidant, corresponding to 83.4 ± 3 percent of the

stoichiometric yield.[8,11] The rate curves were qualitatively similar to those obtained by previous investigators with Q values (mm^3O_2/hr/mg chl a) of approximately 2000.[11] The cells were completely unable to evolve oxygen with carbon dioxide as oxidant subsequent to completion of the Hill reaction.[8] The pH of the suspensions was not changed by more than 0.02,[11] either by completion of the Hill reaction or by addition of 6 T solution, M/3 phosphate buffer, or quinone.

When 0.25-0.50 mg of 6 T was incubated with the algae prior to quinone addition the effect (6 T effect) on the subsequent rate varied from twofold stimulation to nearly complete inhibition. These variations could be correlated with the dependence of the control rate on the concentration of quinone. At low values, when the rate increased with increasing quinone concentration, the 6 T effect was consistently stimulatory (44 experiments). At high concentrations, when the rate was self-inhibited by quinone and/or its photoproducts, the 6 T effect was an increase in the inhibition (17 exp.).[8,12] At intermediate concentrations no effect (rate within 5 percent of control) was observed. The numerical concentrations at which each of these effects appeared in turn depended upon the light intensity, suspension density, chlorophyll content, incubation conditions, and culture conditions as described below.

There was no significant alteration in the yield of oxygen in the presence of 6 T. Table I, which summarizes the data on Scenedesmus in all experiments where quinone was not self-inhibitory, indicates that the amount of oxygen attributable to 6 T is less than 5 percent of what would be expected if it were acting as a Hill oxidant (54 mm^3/mg 6 T). Such a result is consistent with separate experiments in which 1 mg 6 T was incubated with algae (in the absence of quinone to inactivate them photosynthetically) and also with quinone in the absence of algae. The subsequent yields of photochemical oxygen were 12 and 3 mm^3O_2/mg 6 T respectively.

Chemical Specificity

If the observed rate effects are the result of a change in the concentration of the 6 T quantum converter within the cell, and not merely a chemical artifact, addition of the 4 T and 5 T which do not possess the ring-strain energy required for quantum conversion should have no effect.[1] 6 MD and 6 DT, however, which might be easily converted to 6 T biosynthetically,[13] might behave in a manner similar to 6 T. In a standard dark incubation experiment, under conditions in which 6 T gave 50 percent stimulation, neither 5 T, 4 T, 6 MD nor 6 DT in the same molar concentration (0.0005 M) produced any effect (Fig. 1A).

To test whether more active metabolism would facilitate conversion of 6 DT and 6 MD to photoactive 6 T, incubation was carried out aerobically in light (26,000 lux) for 1/2 hour. The subsequent rates were essentially identical with the dark-incubated rates, wtih the exception of a small stimulatory effect by 6 DT after light incubation (Fig. 1B).

Although there was no appreciable alteration of the rate by 6 DT, the average yield was 13 ± 3 mm^3O_2/0.25 mg 6 DT less than in the controls (4 exp.). The decrease calculated for a one-to-one reaction of 6 DT and quinone, such as a dark reduction of the latter, is 13.4 mm^3O_2/0.25 mg 6 DT. A non-reversible reaction with quinone which inactivates the dithiol-disulfide system may explain the lack of Hill activity of 6 DT.

Thioctic Acid Concentration and Metabolic Requirement

The total of free and combined forms of 6 T in Scenedesmus is quite small, approximately 10^{-8} gms/40 mm^3 cells,[14] and presumably the photoactive form in the "photosynthetic unit"[15,16] is only a small fraction of that amount. Although in principle it should require only a few-fold increase in the amount of the photoactive form to give rise to the observed effects on the Hill reaction, the stimulation in a typical experiment drops off rapidly when the amount of added 6 T is less than 10^{-4} gm/40 mm^3 cells (Fig. 2).

There is evidence that in its other metabolic functions, 6 T is present in specific bound forms, such as lipothiamide pyrophosphate.[17] This may be the case when it functions in the quantum conversion process, and the biosynthesis of such a form from externally supplied 6 T might be slow and require both oxidative metabolism and the relatively high concentration of exogenous 6 T actually observed.

To test the possible dependence of the 6 T effect upon oxidative metabolism, equal aliquots of 6 T solution were added to algae at the beginning of the dark-adaptation period, just before the dark aerobic shaking, just after the N_2 flush, mixed with quinone, and ten minutes after quinone addition (Fig. 3). The preparatory reactions are essentially complete within 10 minutes in air, but are not accomplished in N_2 or by quinone-killed algae, supporting the concept that the molecule must be metabolically prepared for its photoactive function.

Quinone Concentration

Although the control rates varied considerably with the particular harvest of algae, certain characteristics of the effect of the quinone concentration on the 6 T effect were common to most samples tested (Fig. 4). At sufficiently low quinone concentrations the control rate varied directly though not linearly with the quinone concentration. It is in this concentration range that the 6 T effect is stimulatory, lower concentrations yielding higher percentage but less accurately measured stimulations. As the concentration of quinone in the control is increased, a maximum rate is obtained; higher concentrations of quinone result in lower rates.[8] When the quinone concentration is increased in 6 T incubated algae, a maximum rate is also obtained, but at a somewhat lower quinone concentration and with a more rapid decrease in rate at higher concentrations than in the control. An important characteristic of the 6 T effect is that the maximum rate with 6 T is nearly identical to the maximum without it.

The existence of quinone-saturated rates indicates that there are one or more quinone-independent rate-determining steps in the Hill reaction sequence. If 6 T were to act on one or more of these other slow steps, then it should yield, assuming microscopic reversibility of the reactions, a maximum stimulated rate considerably higher than that obtainable by saturating the quinone-dependent rate-determining reaction alone. If on the other hand 6 T acts upon the quinone-dependent step, the maximum stimulated and maximum control rates should be nearly identical, the former possibly slightly higher if at these concentrations the quinone partially inhibits some other reaction in the sequence. The available evidence therefore supports the idea that 6 T acts upon the quinone-dependent step.

Mechanism of Inhibition

Although the inhibitory effects of high quinone concentrations and preilluminated quinone are established observations,[8,11,12] there is at present little information as to the chemical species involved. If 6 T is the direct reductant of quinone in the Hill reaction, a photolysis product of quinone of somewhat similar structure might enter into a nonreversible reaction with the natural 6 T destroying the quantum conversion mechanism and possibly inhibiting other reactions in the Hill reaction sequence.

To test the effect of photolytic products of quinone on the 6 T effect, aliquots of quinone solution and quinone plus 6 T were illuminated in nitrogen for thirteen minutes before use in the standard experiment (Fig. 5). Illumination of the quinone produced the previously described inhibition.[8,11] While the concentration of quinone was low enough to yield a twofold 6 T stimulation in the control, preillumination of the quinone changed the effect to nearly complete inhibition. When quinone and thioctic acid were preilluminated together, however, the inhibition was less than with quinone preilluminated alone. Incubation with 6 T thus does sensitize the cells in some way to inhibition by photolyzed quinone and it is probable that the observed instances of an inhibitory 6 T effect at high quinone concentrations result from such an interaction.

It may be well to point out that the observed inhibitions were not caused by a net destruction of the quinone. When the latter was illuminated, a broad u.v. absorption band slowly appeared whose optical density increased approximately linearly with time. The optical density after 13 minutes was found to be less than one percent of the value after 90 minutes in the standard light field followed by 90 minutes in the light from a bank of black lights (u.v.). The most obvious conclusion is that the fraction of quinone destroyed in the preillumination period was also less than one percent. The photoproducts would then be toxic in a concentration of $< 4 \times 10^{-5}$ M.

Light Intensity

The effect of light intensity on the 6 T effect is closely related to its role in the photolysis of quinone and as a partially rate-determining step in the Hill reaction sequence.[18] The former effect results in inhibitory 6 T effects at very high intensities.[12,19]

The second effect is exactly what would be expected from a partially rate-controlling step which is independent of 6 T. An increase in the quantum capture rate induced by an increase in the light intensity will increase the dependence of the net Hill rate on the quinone concentration. Saturation of the capture process at higher light intensities corresponds to the greatest dependence of the Hill rate upon quinone concentration and therefore coincides with the greatest percentage stimulations by 6 T. In several experiments a third rate-determining step, as yet unidentified, proved slower than either the quinone-dependent or quantum capture steps, and since in these instances light saturation did not correspond to quinone dependence no stimulatory 6 T effect was observed.

Although saturation of the capture process was not a sufficient condition for stimulation, it was a necessary one. After conditions were found which yielded a stimulatory 6 T effect, the incident light intensity was reduced

to 33 percent, resulting in a lower percentage stimulations or slight inhibitions. The existence of these inhibitions indicates that the net 6 T effect is the resultant of both a stimulatory and an inhibitory effect which have different dependences on the quinone concentration and light intensity (Fig. 6).

Suspension Density

The quantity of cells present in the manometer vessels determines the quantitative dependence of the control rate on light intensity and quinone concentration, and therefore the 6 T effect, in several ways.[18] At low suspension densities the Hill rate becomes saturated with respect to both quinone and light, and there is no 6 T stimulation. If the concentration of quinone is sufficiently high the photolysis products formed result in 6 T inhibition. As the density is increased, an increasing fraction of the incident light is captured, the average light absorbed per alga decreases, the dependence of the net Hill rate on light increases, and the net effect is to decrease the possibility of a stimulatory 6 T effect. On the other hand, while at a particular algal density the relative quinone concentration determines quinone dependence, the quinone-algae ratio determines the actual concentration range of this dependence. Hence the dependence of the control rate on quinone increases with the suspension density, and an increase in the latter increases the possibility of a stimulatory 6 T effect.

The observed 6 T effect is the resultant of these two opposing effects whose magnitudes are sensitive functions of the physiological state of the algae. Fortunately, under the present culture conditions, Scenedesmus becomes quinone dependent before light dependent as the suspension density is increased, and a region of net stimulatory 6 T effect is observed at intermediate densities, with no effect at higher and lower densities (Figs. 7A and 7B).

Culture Conditions and Chlorophyll Content

The physical conditions under which the algae are cultured in part determines the relative contributions of the rate-determining steps in the Hill reaction. As these conditions are adjusted to produce algae with a relatively low chlorophyll content, it becomes more difficult to saturate the quantum capture step, the algae become light dependent more rapidly than quinone dependent, and the net effect is that at no algae density is a stimulatory 6 T effect observed. Such "pale algae" (30-75 percent of the standard, ca. 6×10^{-3} mg chl a/mm^3 cells) were developed by decreasing the inoculum size (to ca. 10 percent) following each harvest, and not allowing the culture cell density to become large (standard ca. 4 mm^3/ml). Under these conditions the algae developed at a higher average light intensity because of a decrease in the light shielding by other algae in the light path. Such algae appeared to adjust to their environment by developing an efficient quantum conversion system at the expense of the capture system, and failed to exhibit either light saturation or 6 T stimulation of the Hill reaction under the present experimental conditions.[20]

When the algae were cultured under low incident-light intensities (33 percent standard) they appeared to adapt to a lower rate of photosynthesis and become saturated with respect to both quinone and light at the lowest convenient concentration of the former (0.8 mg/40 mm^3 cells), and thus exhibit no stimulatory 6 T effect.

Other Biological Systems

If the quantum conversion theory possesses the generality which it claims, it should be possible to realize stimulatory 6 T effects in other plants. However, Chlorella pyrenoidosa cultured under the same light and gas phase conditions as Scenedesmus repeatedly failed to exhibit any but inhibitory or nil 6 T effects (Fig. 8). These algae developed considerably less chlorophyll/mm^3 cells than Scenedesmus under the same culture conditions (ca. 4×10^{-3} mg chl a/mm^3 cells), and behaved in a manner similar to "pale" Scenedesmus, being quinone independent and, generally, highly light dependent. Stimulatory thioctic effects are not to be expected under these conditions, and we have as yet been unable to find growth conditions which develop Chlorella with a sufficiently high chlorophyll content to obtain quinone dependence and light saturation under the present Hill conditions.

Several experiments with Synechococcus cedorum which were cultured under lower light intensities also resulted in inhibitory 6 T effects. As in the case of "pale" Scenedesmus and Chlorella, the control rates were quinone saturated and light dependent.

Discussion

There are many a priori possible mechanisms by which 6 T may affect the Hill reaction. Fortunately it is possible to eliminate a number of them on the basis of the data available. The experiments with illuminated quinone solutions give strong support to the idea that an interaction between one or more quinone photoproducts and 6 T to produce an extremely toxic material, possibly the same moiety which is active in ordinary "self-inhibition" by quinone, is primarily responsible for the observed instances of 6 T inhibition.

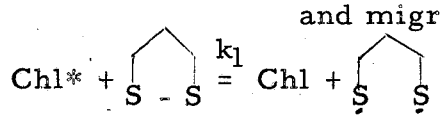
It is also possible to draw rather general conclusions as to the mechanism responsible for the observed instances of stimulation. The failure to observe oxygen evolution when 6 T is incubated separately with either algae or quinone rules out the possibility of any simple two-component process. The fact that 6 T does not contribute to the oxygen yield of quinone further indicates that it is not acting as a Hill oxidant in the ordinary sense, and that the stimulatory effect is not simply the result of an increase in the total concentration of oxidants at the site of reduction. In addition, it is unlikely that the effect involves either a pH change or a reversal of self-inhibition by quinone, since under conditions in which the latter is considerably self-inhibitory 6 T is more so.

As has been discussed previously, the fact that the maximum thioctic-stimulated rate is nearly identical with the maximum control rate indicates that 6 T acts on the quinone-dependent step in the Hill sequence. Presumably, the only reactions which are quinone dependent involve either transport of the quinone to the reduction site or the actual reduction process itself. It seems unlikely, for example, that the systems for evolving oxygen or transporting hydrogen to the chloroplast would depend on the quinone concentration. It seems equally improbable that 6 T would stimulate the transport of quinone to the reduction site, which appears to be very close to the chlorophyll.[21] If, then, the 6 T effect is on the reduction process itself, either a change in the actual mechanism or an increase in the concentration of the reductant at the reduction site may be responsible for the observed stimulation. Such an increase in

reductant concentration could be brought about if 6 T acted as a hydrogen transport system from a primary reductant associated with the chloroplast to the quinone reduction site. Receiving hydrogen from reduced DPN, carrying it to the reduction site, and reducing the quinone directly might be the 6 T function.[2] Such a function would depend upon the unique character of the 6 T five-membered ring since 4 T and 5 T are inactive. It is difficult, however, to reconcile this mechanism with the apparent resistance of the 6 T to net reduction as a Hill oxidant, together with the experimental observation that when it acts in pyruvic acid oxidation it functions in the reverse manner, i.e. the 6 DT reduces oxidized DPN.[22] Finally soluble reduced DPN is apparently absent from illuminated washed chloroplasts, which reduce quinone, for they fail to activate the malic enzyme system.[23,24,25] The latter evidence indicates that pyridine nucleotides are not required for reduction of quinone in chloroplasts.

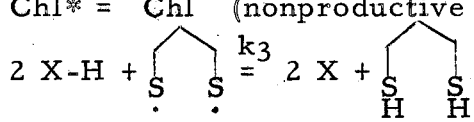
The quantum conversion theory provides a unique mechanism by which the quinone reductant concentration may be increased by 6 T. The process involves a sequence of reactions such as:

$$\mathrm{Chl} + h\nu \overset{k}{=} \mathrm{Chl}^*$$ (light absorption and quantum transformation and migration.)



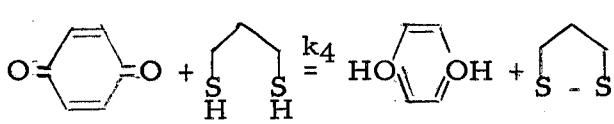
(quantum conversion process)

$$\mathrm{Chl}^* \overset{k_2}{=} \mathrm{Chl}$$ (nonproductive decay)



$$X \rightarrow Y \rightarrow Z \rightarrow \cdots\cdots = O_2$$

$$H_2O \rightarrow A \rightarrow B \rightarrow C \rightarrow \cdots\cdots = XH$$



in which the hydrogen donor, XH, is produced by a series of reactions from water; the oxidized product, X, is ultimately the source of oxygen evolved; and nonproductive decay includes fluorescence, nonradiative thermal decay to the ground state, etc. 6 T provides the rather unique function of increasing the reduction level of the transferred hydrogen by an amount corresponding to some fraction of the energy difference between the oxidized form and the diradical, the remaining fraction being used to raise the oxidation level of the oxygen-containing residuum, X.

The rate laws associated with this process may be formulated as:

$$\frac{d\,\mathrm{chl}^*}{dt} = k(I)(\mathrm{chl}) - k_1(\mathrm{chl}^*)(S - S) - k_2(\mathrm{chl}^*)$$

$$\frac{d\,S - S}{dt} = k_4(SH)(Q) - k_1(\mathrm{chl}^*)(S - S)$$

$$\frac{d\,S^{\cdot}}{dt} = k_1(chl^*)(S - S) - k_3(X - H)^2(S^{\cdot})$$

$$\frac{d\,SH}{dt} \quad k_3(X - H)^2(S^{\cdot}) - k_4(Q)(S - H)$$

$$\frac{d\,Q}{dt} = -k_4(Q)(S - H)$$

where (I) is the incident light intensity, (S - S) the concentration of 6 T, (SH) that of 6 DT, ($S^{\cdot}$) that of the diradical, (Q) that of quinone. For convenience, $m \cong (S - S) + (S^{\cdot}) + (SH)$.

The observed dependence of 6 T stimulation effect upon light intensity and quinone concentration is consistent with the proposed model. The general form of this dependence may be seen without resorting to an exact solution of the differential rate equations in the restricted case of the steady state. Under this restriction the concentration of all intermediates remains constant throughout the course of the reaction, and in addition $dQ/dt = -2dO_2/dt$. Since the concentration of quinone decreases continuously as the reaction proceeds, this steady state assumption cannot be completely valid. However, since m is several orders of magnitude smaller than the quinone concentration, the system will adjust itself to changes in quinone concentration extremely rapidly, and conclusions deduced on the steady-state model will apply for each manometer reading, although not a sequence of them.

The effect of added 6 T, i.e. an increase in m, depends upon the value of K, defined as

$$\frac{k_1(S - S)}{k_2 + k_1\,(S - S)} \cong K$$

and which corresponds to the fraction of quanta used productively. Whenever K is significantly less than unity additional 6 T will stimulate the net reaction. At sufficiently low light intensitites the net rate will become completely light dependent, and the steady state values of ($S^{\cdot}$) and (SH) will become small so that (S - S) = m. (A quantative analysis may be found in the Appendix.) If $k_1 m \gg k_2$ then, K is nearly unity and there will be no 6 T effect. If $k_1 m \ll k_2$, K will approach zero, and the 6 T effect will be stimulatory. As the light intensity is increased indefinitely, some other reaction such as quinone reduction will become partially rate determining, ($S^{\cdot}$) and (SH) will become appreciable and K will decrease. Increasing m by added 6 T will increase (S - S) by a fraction of m which depends on the actual values of the rate constants involved, K will increase and the thioctic effect will be stimulatory. 6 T increases (S - S) by speeding up the assumed rate determining step, $k_4(SH)(Q)$ and therefore an increase in quinone will have the same effect.

If K at quinone saturation is unity then the maximum thioctic-stimulated rate will equal the maximum quinone-stimulated rate. If not, then 6 T will result in a higher maximum rate, corresponding to the direct stimulation of two partially rate-determining steps, quantum conversion and quinone reduction. The observed correspondence of the two rates indicates that it is only the latter reaction which is being stimulated directly and that therefore at quinone saturation there is negligible nonproductive decay.

As there is no a priori reason that the quinone reduction is a slower reaction than diradical reduction, it would not be surprising to find that the physiological state of the particular plant sample which determines the relative rate constants of these reactions would also determine the dependence of the 6 T effect on quinone concentration. It is, of course, in principle possible to observe 6 T stimulation if quinone is not rate determining provided that the diradical reduction may be stimulated by an increase in (S·). If the reduction of XH is absolutely limited, however, then the 6 T effect cannot be stimulatory. Therefore, quinone dependence is a sufficient but not necessary condition for stimulation, while light saturation is not a sufficient condition and only a necessary one in the case of a naturally low quantum decay rate.

Summary

1. Conditions have been realized under which the Hill reaction by cellular chloroplasts of Scenedesmus is stimulated by prior incubation with synthetic 6-thioctic acid.

2. The conditions for stimulation are sensitive functions of the oxidant concentration, 6-thioctic acid concentration, light intensity, suspension density, chlorophyll content of the algae, culture conditions, and incubation condition.

3. The three most general experimental conditions for stimulation are: a) dependence of the Hill control rate on oxidant concentration, b) saturation of the control rate with respect to light intensity, and c) incubation of algae with 6-thioctic acid aerobically prior to oxidant addition. The second and third conditions are necessary, the first is sufficient.

4. Under conditions in which quinone is self-inhibitory, the 6-thioctic acid is also inhibitory.

5. The observed stimulatory effects are consistent with the proposal that 6-thioctic acid is the primary quantum converter in photosynthesis.

Appendix

In the steady state solution R, defined as:

$R \cong$ net steady state rate of Hill reaction,

is also equal to the rate of every individual reaction in the sequence. We may therefore express the concentrations of the reactants in terms of R.

$$R = k_4(SH)(Q)$$

$$R = k_3(XH)^2(S\cdot)$$

$$\text{and } R = k'K \cong \frac{k'k_1(S - S)}{k_2 + k_1(S - S)}$$

where $k' \cong kI(chl)$

Using the additional relation

$$m = (S - S) + (S\cdot) + (SH)$$

(SH), (S·) and (S - S) may be eliminated and R expressed as a function of m:

$$R = \frac{m + \frac{k_2}{k_1} + \frac{k'}{k_4(Q)} + \frac{k'}{k_3(XH)^2} \pm \sqrt{\left(m + \frac{k_2}{k_1} + \frac{k'}{k_4(Q)} + \frac{k'}{k_3(XH)^2}\right)^2 - \frac{4\,mk'}{k_4(Q)} - \frac{4\,mk'}{k_3(XH)^2}}}{\frac{2}{k_4(Q)} + \frac{2}{k_3(XH)^2}}$$

The physically significant root may be expanded in a power series to yield, for the leading terms,

$$R \cong \frac{mk'}{m + \frac{k_2}{k_1} + \frac{k'}{k_4(Q)} + \frac{k'}{k_3(XH)^2}} + \frac{\left(\frac{1}{k_4(Q)} + \frac{1}{k_3(XH)^2}\right) m^2 k'^2}{\left(m + \frac{k_2}{k_1} + \frac{k'}{k_4(Q)} + \frac{k'}{k_3(XH)^2}\right)^3} + \cdots$$

The limiting cases of interest are summarized below:

limit	R
$Q \to 0$	$k_4 m Q$
$\begin{cases} Q \to \infty \\ (XH)^2 \to \infty \end{cases}$	$\frac{mk_1k'}{mk_1 + k_2}$
$I \to 0$	$\frac{mk_1k'}{mk_1 + k_2}$
$I \to \infty$	$\frac{m}{\frac{1}{k_4(Q)} + \frac{1}{k_3(XH)^2}}$
$m \to 0$	$\frac{mk'}{\frac{k_2}{k_1} + \frac{k'}{k_4(Q)} + \frac{k'}{k_3(XH)^2}}$
$m \to \infty$	k'

References

1. M. Calvin and J. A. Barltrop, J. Am. Chem. Soc., 74, 6153 (1952).

2. W. Vishniac and S. Ochoa, J. Biol. Chem., 198, 501 (1952).

3. M. Goodman, D. F. Bradley, and M. Calvin, J. Am. Chem. Soc., in press.

4. B. L. Strehler, "Phosphorus Metabolism," II, Johns Hopkins Press, Baltimore, 1952.

5. H. Gaffron and E. W. Fager, Ann. Rev. Plant Physiology, 2, 87 (1952).

6. A. A. Benson, M. Calvin, V. A. Haas, S. Aronoff, A. G. Hall, J. A. Bassham, and J. W. Weigl, "Photosynthesis in Plants," Chapt. 19, 381-401. Iowa State College Press., Ames, Iowa, 1949,

7. L. Jacobson, Plant Physiol., 26, 411 (1951).

8. K. A. Clendenning and H. C. Ehrmanstraut, Arch. Biochem., 29, 387 (1950).

9. P. R. Gorham and K. A. Clendenning, Arch. Biochem. Biophys., 37, 199 (1952).

10. E. I. Rabinowitch, "Photosynthesis and Related Processes," II, Part 1, Chapt. 21. Interscience, New York, 1951.

11. D. I. Arnon and F. R. Whatley, Arch. Biochem., 23, 141 (1949).

12. H. C. Ehrmantraut and E. Rabinowitch, Arch. Biochem. Biophys., 38, 67 (1952).

13. G. R. Seaman, J. Biol. Chem., 200, 813 (1953).

14. R. C. Fuller, private communication.

15. R. Emerson and W. Arnold, J. Gen. Physiol., 16, 191 (1932).

16. J. B. Thomas, O. H. Blaauw, and L. N. M. Duyzens, Biochem. Biophys. Acta, 9, 575 (1952).

17. L. J. Reed and B. G. DeBusk, J. Biol. Chem., 199, 881 (1952).

18. E. I. Rabinowitch, "Photosynthesis and Related Processes," II, Part 1, Chapt. 28, Interscience, New York, 1951.

19. E. S. Nielsen, Physiol. Plantarum, 5, 334 (1952).

20. E. I. Rabinowitch, "Photosynthesis and Related Processes," I, Chapt. 15, Interscience, New York, 1945.

21. Y. G. Shiau and J. Franck, Arch. Biochem., 14, 253 (1947).

22. L. J. Reed and B. G. DeBusk, J. Am. Chem. Soc., 75, 1261 (1953).

23. W. Vishniac and S. Ochoa, Fed. Proc., in press, 1952.

24. L. J. Tolmach, Arch. Biochem., 33, 120 (1951); Nature, 167, 946, 768 (1951).

25. E. Rabinowitch, Ann. Rev. Plant Physiol., 3, 229 (1952).

Table I

Contribution of 6 T to oxygen evolution

mm^3O_2/mg quinone (controls, 67 exp.)	86.1
mean deviation	3.2
standard error of the mean	0.5
mm^3O_2/mg quinone (+ 6 T, 54 exp.)	87.0
mean deviation	3.2
standard error of the mean	0.6
mean mg 6 T/mg quinone (+ 6 T)	0.36
Stoich. mm^3O_2/mg quinone if 6 T is oxidant	19.6
Observed mm^3O_2/mg quinone if 6 T is oxidant	0.9 ± 0.7

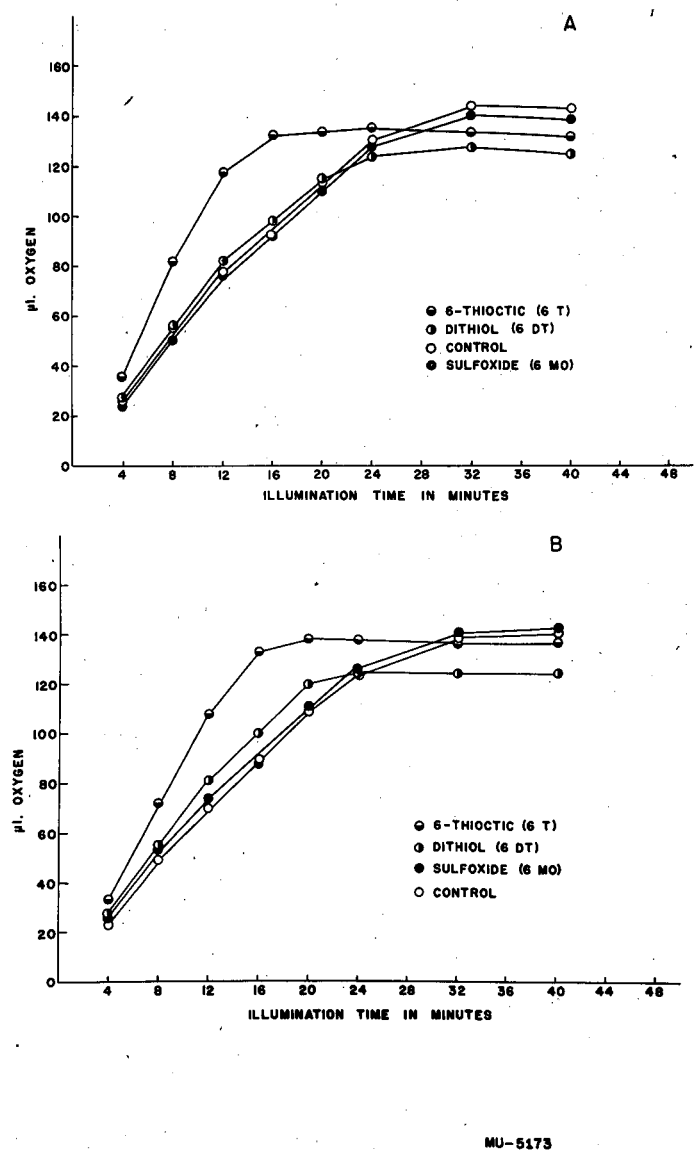
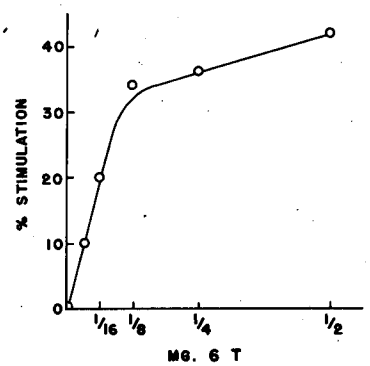


Fig. 1

Chemical specificity of 6 T. 40 mm^3 Scenedesmus and 1.5 mg quinone per vessel. 0.25 mg 6 T, 6 MD, 6 DT when used. A) Standard dark incubation, B) Light incubation.



MU-5177

Fig. 2

6T effect as a function of 6 T concentration. 30 mm^3 Scenedesmus and 1.4 mg quinone per vessel. Standard dark incubation.

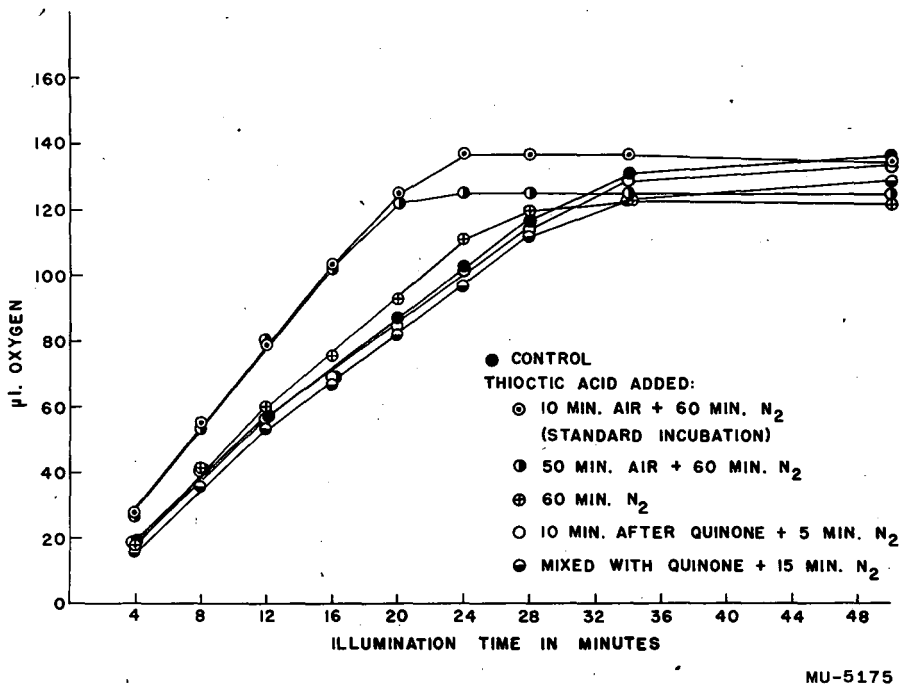
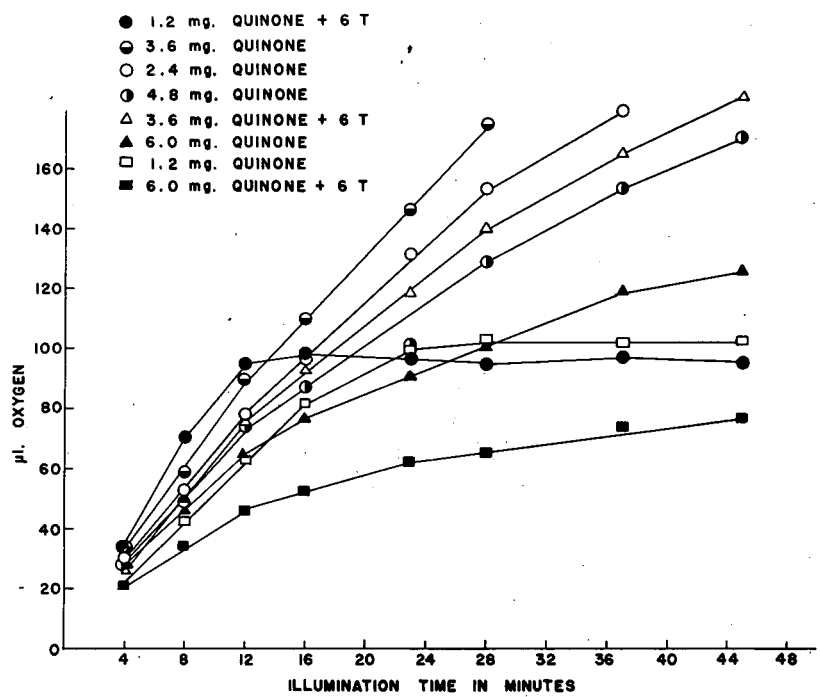


Fig. 3

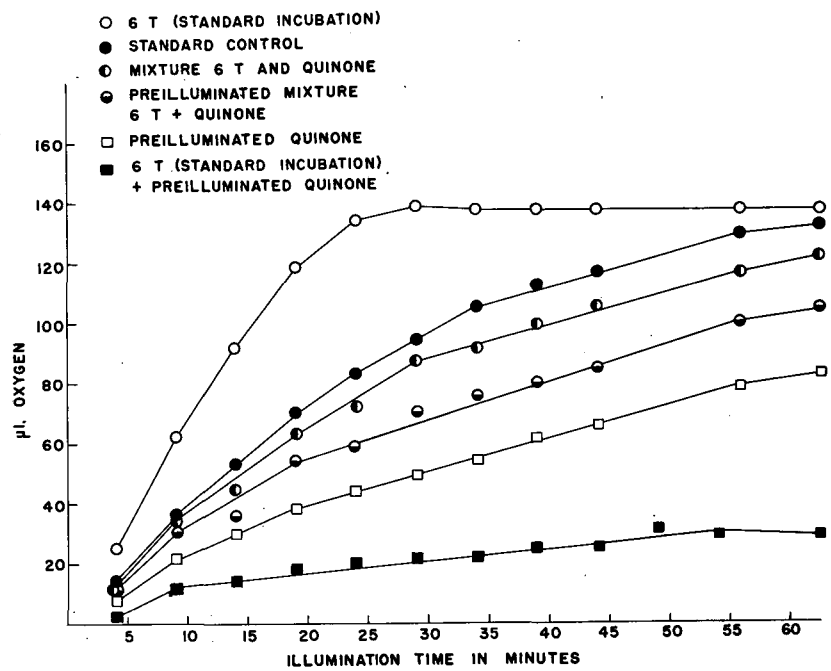
6 T effect as a function of incubation conditions. 40 mm^3 Scenedesmus and 1.5 mg quinone per vessel. 0.25 mg 6 T when used.



MU-5176

Fig. 4

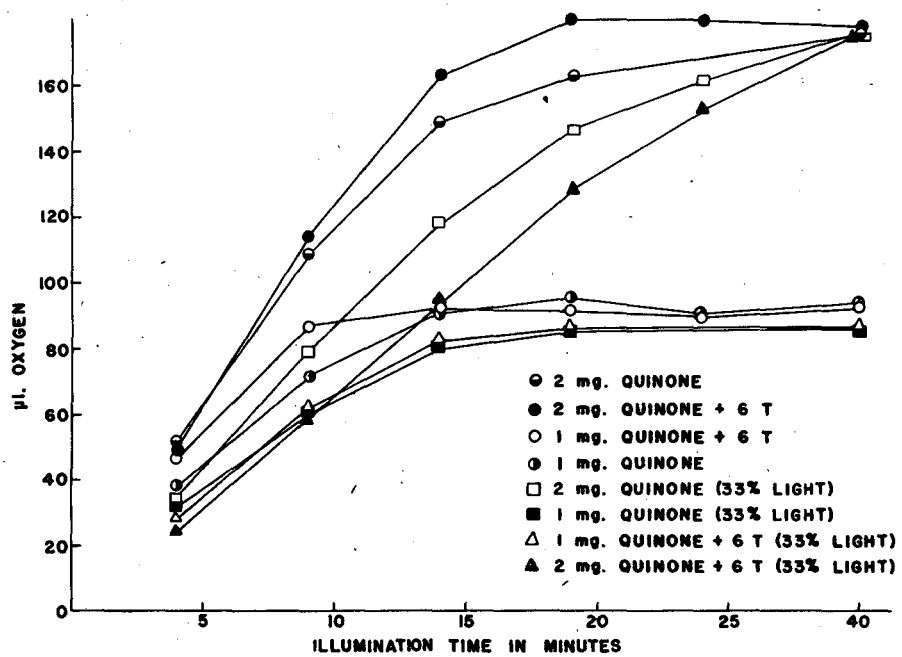
6 T effect as a function of quinone concentration. 40 mm^3 Scenedesmus per vessel. 0.25 mg 6 T when used. Standard dark incubation.



MU-5178

Fig. 5

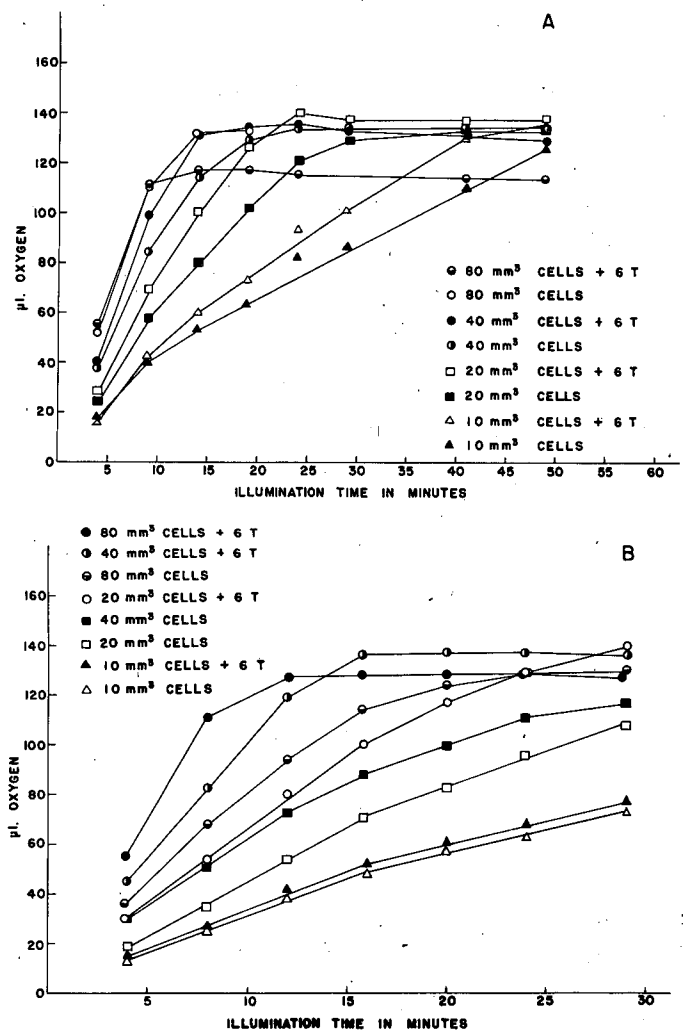
6 T effect as a function of quinone preillumination. 20 mm^3 Scenedesmus and 1.5 mg quinone per vessel. 0.5 mg 6 T when used.



MU-5179

Fig. 6

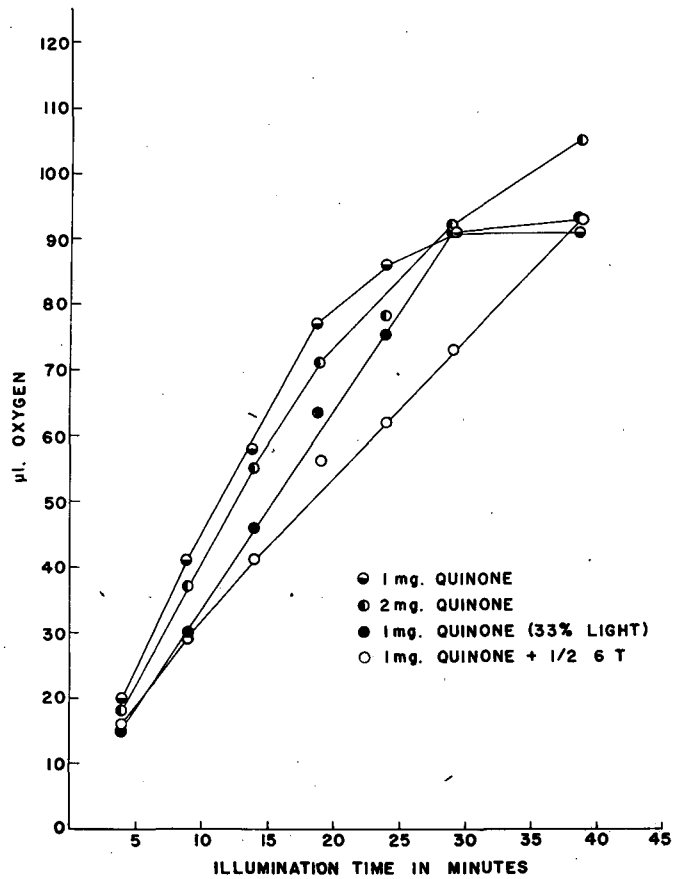
6 T effect as a function of light intensity. 40 mm^3 Scenedesmus per vessel. 0.5 mg 6 T when used. Standard dark incubation.



MU-5174

Fig. 7

6 T effect as a function of suspension density. Scenedesmus and 1.5 mg quinone per vessel. A) 0.25 mg 6 T when used, B) 0.5 mg 6 T when used.



MU-5180

Fig. 8

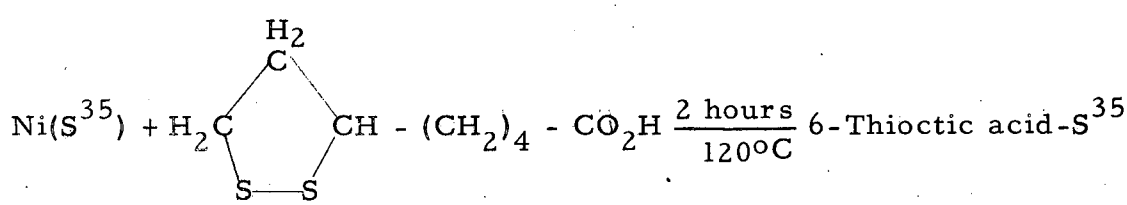
6 T effect in Chlorella. 20 mm^3 cells per vessel.
0.5 mg 6 T when used. Standard dark incubation.

SULFUR^{35}-LABELED 6-THIOCTIC ACID

A. A. Benson

The importance of thioctic acid (lipoic acid, P.O.F., protogen) in metabolic systems, in addition to its proposed function as a primary energy converter in photosynthesis,[1] prompted efforts towards its synthesis with C^{14} and S^{35}. Presumably, the methods ordinarily applicable to its synthesis could be used for the introduction of labeled atoms.

A more direct introduction of the label involves exchange with elemental S^{35} followed by separation of the products. 6-Thioctic acid was found to exchange with S^{35} in the presence of Raney nickel catalyst. Separation of the reaction mixture was accomplished by one-dimensional paper chromatography. Identification of the radioactive product as 6-thioctic acid was done by a variety of known chemical and biological transformations. Chemical transformations provided proof of the S-S cyclic structure, while biological conversion was necessary to prove the position of the trimethylenedisulfide ring in the C_8 chain of the initial reactant.



Exchange was not observed without adding Raney nickel. Exchange of S^{35} with a wide variety of other compounds has been attempted. Though the yields have been low the possibilities of this synthetic route must not be overlooked.

Attempts at exchange of 4- and 5-thioctic acid with S^{35} resulted in isolation of what is believed to be 6-thioctic acid. Such isomerization of secondary sulfide groups is not surprising and the five-membered ring formation has been observed to occur readily in the presence of zinc ion. Ring closure to the five-membered ring might then be expected with a nickel-catalyzed reaction.

Experimental Method

To a solution of 500 μc S^{35} in 0.10 ml ethanol was added 0.5 mg Raney nickel catalyst. After addition of 0.5 mg 6-thioctic acid the ampoule was flushed with nitrogen and sealed. It was heated two hours at 120° with frequent agitation and then cooled and opened. Aliquot portions were chromatographed on Whatman No. 4 paper in n-butanol saturated with 0.5 N ammonium hydroxide. The radioactivity consisted largely of thioctic acid, whose position was identical with that of the carrier, R_f 0.5 (platinic iodide spray test), and unexchanged S^{35}, R_f 0.95. Chromatography of the product in butanol-propionic acid-water and in butanol-ethanol-water also showed the radioactive product corresponding exactly with the authentic material and not with 5- or 4-thioctic acid, whose R_f's are greater in butanol-ammonia. Some improvement in the

1 M. Calvin and J. A. Barltrop, J. Am. Chem. Soc., 74, 6153 (1952).

exchange yield was observed when the mixture was heated at 140° for 20 hours. Equal radioactivity was observed in the S^{35} spot and in the 6-thioctic acid product. However, the separation of S^{35} from the product was not so readily accomplished in a single chromatogram, and it is felt that a lower temperature may be advisable.

Sulfoxide

The product, eluted with chloroform-methanol, was oxidized with dilute permanganate to the sulfoxide and chromatographed in butanol-ammonia with an R_f of 0.25 corresponding to the platinic iodide spray test for authentic sulfoxide.

Disulfonate

More severe oxidation with perpropionic acid (24 hours, 20° C) gave a product with R_f 0 in butanol-ammonia and R_f 0.1 in butanol-propionic acid. This corresponded to that of the disulfonic acid derived from authentic 6-thioctic acid.

Biological Conjugation

Formation of water-soluble conjugates is characteristic of assimilation of thioctic acid by biological systems. Conjugates with thiamin are the coenzyme of pyruvic oxidase. The eluted thioctic acid-S^{35} was incubated one hour with a cell-free enzyme preparation from ultrasonic disintegration of *A. aerogenes*. The product was chromatographed in butanol-propionic acid. Although the majority of the activity was in the band characteristic of thioctic acid and its sulfoxide at R_f 0.9, small amounts of the activity had been converted to conjugates of R_f 0.1 and 0.3. The yield in this conversion may well be low owing to nonradioactive contaminants in the product or to the low activity of the enzyme preparation.

CONTINUATION OF STUDIES ON THE SYNTHESIS OF 6-THIOCTIC ACID

P. T. Adams

Of the two synthetic routes leading to S^{35}-labeled 6-thioctic acid (6,8-dithio-octaonic acid) described in the last quarterly report, the first has been abandoned as completely unsuitable. The second method described was found to produce an unexpected intermediate product and it has therefore been necessary to modify the proposed succeeding reactions.

When ethyl 6-keto, 8-acetylmercapto-octanoate was reduced with sodium borohydride, the reduction product was found to contain a mixture of 6-hydroxy-8-mercapto-octanoate and 6-acetylhydroxy-8-mercapto-octanoate instead of the acetyl mercaptan expected. When the crude mixture from reduction was hydrolyzed in 10 percent potassium hydroxide, 6-hydroxy-8-mercapto-octanoic acid (m.p. 107-8°) was isolated. Attempts to form either the 6-bromo-8-mercapto- or the 6,8-dibromo-octanoate by treatment of any of these hydroxy compounds with thionyl bromide in pyridine resulted only in polymer formation. It has since been reported[1] that 6,8-dibromo-octanoic acid is unstable towards polymerization.

Conversion of the 6-hydroxy-8-mercapto-octanoic acid to the desired 6,8-dimercapto-octanoic acid has been accomplished[2] by treating the hydroxy compound with a large excess of thiourea in refluxing hydrobromic acid, followed by mild alkaline hydrolysis. Attempts are currently being made to alter this procedure so that equimolar amounts of thiourea may be used. In this way, by the use of S^{35}-labeled thiourea, the sulfur-labeled thioctic acid could be obtained.

Meanwhile, another synthetic route involving the intermediate ethyl 7-octenoate, is being investigated. The unsaturated ester has been prepared in the following manner. Ethyl hydrogen azelate was prepared by heating diethyl azelate with azelaic acid for 5 hours at 280° C. The silver salt of the half-acid was prepared and treated with bromine in carbon tetrachloride. The 8-bromo octanoic ester was isolated by vacuum distillation. Attempts at dehydrobromination with alkali[3] were unsuccessful; 8-hydroxy-octanoic acid was isolated in almost quantitative yield. However, treatment of the bromo ester with triethylamine at 100° for 15 hours results in a product which is almost surely the desired octanoic ester, although purification and identification are not yet complete.

Hornberger's recent article (loc. cit.) describes the preparation of 6-thioctic acid from 4-(α-tetrahydrofuryl)-butyric acid. The acid is treated with a refluxing hydrobromic acid-sulfuric acid mixture to form the lactone of 8-bromo-5-hydroxy-octanoic acid. This lactone, however, under the influence of heat and acid, expands and contracts to form a mixture of 4,8- 5,8-, and 6,8- substituted compounds. Subsequent treatment with thiourea in refluxing hydrobromic acid followed by alkaline hydrolysis and mild iodine

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1 Hornberger et al, J. Am. Chem. Soc., 75, 1273 (1953).
2 Bullock et al, J. Am. Chem. Soc., 74, 3455 (1952).
3 Org. Syn. Coll. Vol. I, p. 209.

oxidation forms the mixed 4-, 5-, and 6-thioctic acids. Therefore separation of isomers in the final product is of primary importance.

Hornberger's synthesis has been duplicated here in order to obtain a supply of the thioctic acids for experimental purposes. Furfural and acetaldehyde were condensed in aqueous base to give furan-acrolein, which was hydrogenated over Raney Nickel to give 3-(α-tetrahydrofuryl) propanol. The alcohol was treated with thionyl chloride and the ensuing tetrahydrofuryl propyl chloride was converted to the Grignard reagent and carbonated with CO_2 to form the 4-(α-tetrahydrofuryl)-butyric acid. The acid was treated with a refluxing mixture of hydrobromic acid and sulfuric acid, the bromo-lactone extracted into chloroform, and the solvent distilled to dryness. The crude bromo-lactone was then treated with 2 molar equivalents of thiourea in refluxing hydrobromic acid for 16 hours. The reaction mixture was neutralized with sodium carbonate and heated at 100° for 15 minutes in 1 percent sodium hydroxide. The hydrolysis solution was acidified, extracted into chloroform and oxidized to the disulfide in dilute chloroform with a slight excess of potassium triiodide solution. The weight of crude total acids corresponds to about 30 percent yield from the tetrahydrofuryl butyric acid. However, bioassay with Streptococcus faecalis (as described in the last quarterly report) showed a yield of less than one percent of the 6,8- isomer. Silicic acid chromatography was found to enrich the concentration of the 6,8- compound to about 10 to 20 percent of the weight of those fractions which show the highest biological activity. Clean separation of the isomers has not yet been accomplished, however. If silicic acid chromatography cannot be made to yield pure products, alumina chromatography of the esters of the thioctic acid will be tried.

SYNTHESIS OF LABELED ORGANIC COMPOUNDS

Doris Chin and R. M. Noller

During the past quarter the following high-specific-activity preparations have been completed (all yields are based on $BaC^{14}O_3$): sodium caproate-1-C^{14}, 13.2 mc in 97 percent yield; ethyl bromoacetate-1-C^{14}, 2.5 mc in approximately 70 percent yield; sodium valerate-2-C^{14}, 30.4 mc in 17.3 percent yield; palmitic-1-C^{14} acid, 15.0 mc in 96 percent yield; and glyceryl tripalmitate-1-C_3^{14}, 4.7 mc in 78 percent yield.

Palmitic-1-C^{14} Acid

Palmitic-1-C^{14} acid (15 mc, 6.05 μc/mg) was prepared from pentadecyl bromide and $BaC^{14}O_3$ by a standard Grignard carbonation. The crude product was purified by extracting its ether solution with water (after decomposition of the excess Grignard reagent with dilute sulfuric acid) and then transferring the palmitic acid to an aqueous phase by addition of a twofold molar excess of KOH solution. The water phase was then extracted with ether until the impurities, which consisted mainly of C_{15} and C_{30} hydrocarbons, were removed. The aqueous phase was then acidified and the palmitic acid extracted back into ether. The ethereal solution was treated with charcoal, dried with anhydrous sodium sulfate, filtered, and evaporated to dryness. The weight yield of palmitic acid from barium carbonate was 96 percent. The specific activity of the product was 6.05 μc/mg, the theoretical specific activity based on the barium carbonate used was 5.57 μc/mg.

Glyceryl Tripalmitate-1-C_3^{14}

A portion of the above palmitic-1-C^{14} acid was used to prepare glyceryl tripalmitate-1-C_3^{14}. Glycerol (119.7 mg, 1.3 mmoles), palmitic-1-C^{14} acid (1000 mg, 3.9 mmoles), and 15 mg of a "mixed alkyl sulfonic acid" catalyst (obtained from Indoil Chemical Products Co., Chicago, Illinois) were placed in a small reaction vessel fitted with an efficient stirrer and a steam-jacketed condenser. The system was evacuated to 25 mm pressure and heated at 125° for three hours. The reaction mixture was then dissolved in petroleum ether and extracted with water. The petroleum ether solution was then dried over sodium sulfate and placed on a 2:1 silicic acid-celite chromatographic column. The tripalmitin was eluted from the column with a solution of 5 percent ether in petroleum ether and the residual dipalmitin and palmitic acid were eluted with ether.

The tripalmitin eluate was evaporated to dryness and the residue dissolved in ether. This solution was treated with "Nuchar", filtered, and evaporated to dryness. The product was recrystallized from ether, giving 855 mg of tripalmitin (81 percent yield based on palmitic acid). The specific activity was 5.53 μc/mg; the theoretical specific activity (based on $BaC^{14}O_3$) was 5.31 μc/mg.

As yet, paper-chromatographic tests of the radiopurity of the labeled palmitic acid and tripalmitin have not been made. Although there may be traces of dipalmitin in the tripalmitin, neither product is likely to have any major radioactive impurity.

THE METABOLISM OF FATTY ACIDS BY PANTOTHENIC-ACID DEFICIENT RATS

Ann M. Hughes and Martha R. Kirk

The production of pantothenic-acid deficient rats (hereafter called "PAD rats") has been described in the Quarterly Report for December, 1952, January and February, 1953. Also the technique for measuring respired $C^{14}O_2$ by passing the breath through an ionization chamber was described in that and previous Quarterly Reports. The studies on the metabolism of $C^{14}H_3COONa$, with and without the injection of Coenzyme A, have been continued and supplemented by similar experiments with $C^{14}H_3(CH_2)_5COONa$. The labeled compound has always been injected intraperitoneally (i.p.). In the studies on the acetate, Co-A was always injected intravenously (i.v.), using the tail vein. In the studies on the heptanoate, the Co-A was injected i.v., i.p., or subcutaneously (subcut.) in the tail. The Co-A injection preceded the labeled compound by 1/2-1 minute. The dosage level for the labeled compound was 2 mg (about 10 μc), and for the Co-A, 4 mg.

$C^{14}H_3COONa$

The results of experiments on the metabolism of the labeled acetate by (1) PAD rats, (2) PAD rats injected with Co-A, and (3) control rats are shown in Figs. 1-4. Fig. 1 gives the percentage recovery of the injected labeled compound. Figs. 2, 3, and 4 show the rate of elimination as $C^{14}O_2$. There is a slight shift in the peak of the curve, but not as obvious as in the case of heptanoate metabolism.

$C^{14}H_3(CH_2)_5COONa$

The results of experiments on the metabolism of the labeled heptanoate by (1) PAD rats, (2) PAD rats injected with Co-A, and (3) control rats are shown in Figs. 5 to 10. Fig. 5 gives the percentage recovery of the injected labeled compound. Figs. 6 to 10 show the rate of elimination as $C^{14}O_2$. The most outstanding difference in the metabolism of the heptanoate by PAD rats with or without Co-A is in the early part of the rate curve. It will be noted that the peak is shifted from 10 minutes (PAD rats) to 25 minutes (PAD rats with Co-A). In the metabolism of the acetate there was no obvious time shift, although there was considerable depression of the early part of the curve. When Co-A is given subcut., the rate is further depressed, becoming almost flat for the period from 10-30 minutes. In the metabolism of heptanoate, an apparent sex difference has appeared in the experiments with subcut. or i.v. injected Co-A. None of the other experiments have shown such a difference. The differences are shown in Table I.

Table I

	% Recovery	
	Male	Female
Co-A i.v.	77.91	69.51
Co-A subcut.	77.97	67.48

A few experiments have been carried out studying the metabolism of heptanoate by control rats injected with Co-A. However, at this time, there are not enough data to report here. Further work will include a continuation of experiments with controls, variations of the amount of Co-A injected, and injections with pantothenic acid and its fragments.

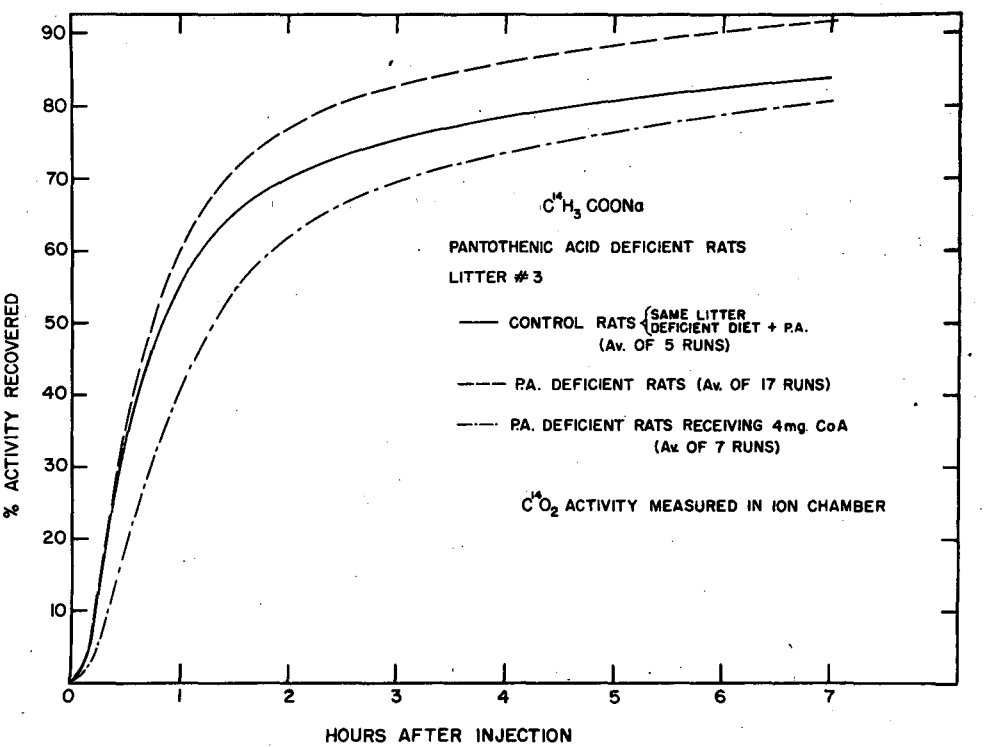
90
80
70
60
50
40
30
20
10
% ACTIVITY RECOVERED
0
1
2
3
4
5
6
7
HOURS AFTER INJECTION
$C^{14}H_3$ COONa
PANTOTHENIC ACID DEFICIENT RATS
LITTER #3
CONTROL RATS {SAME LITTER DEFICIENT DIET + P.A. (Av. OF 5 RUNS)
P.A. DEFICIENT RATS (Av. OF 17 RUNS)
P.A. DEFICIENT RATS RECEIVING 4mg. CoA (Av. OF 7 RUNS)
$C^{14}O_2$ ACTIVITY MEASURED IN ION CHAMBER

FIG. 1

MU - 5723

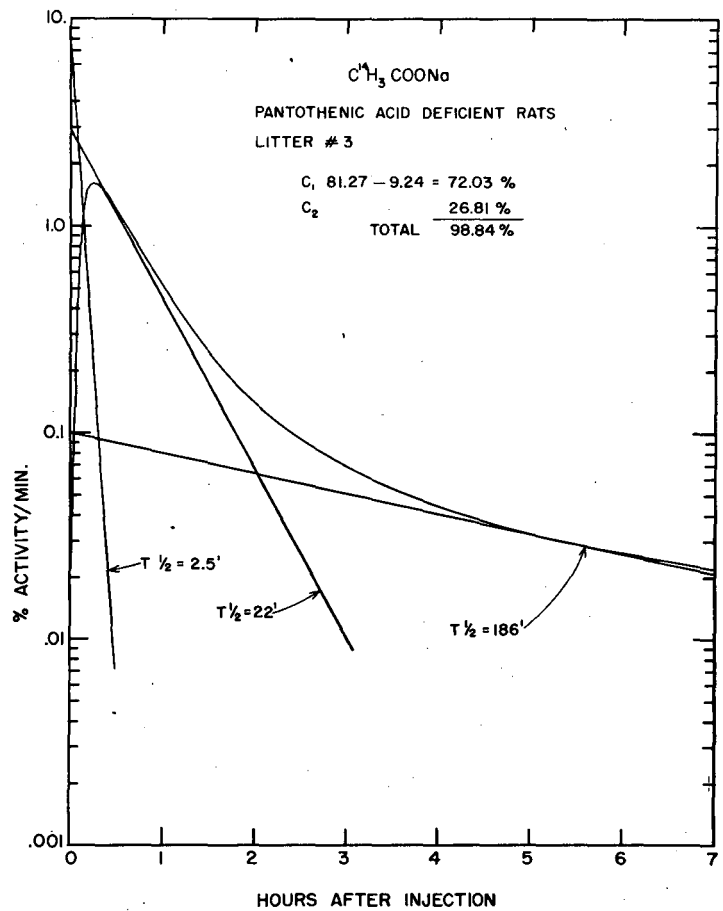
$C^{14}H_3COONa$
PANTOTHENIC ACID DEFICIENT RATS
LITTER #3
C_1 81.27 − 9.24 = 72.03 %
C_2 26.81 %
TOTAL 98.84 %
T ½ = 2.5'
T ½ = 22'
T ½ = 186'
% ACTIVITY/MIN.
10.
1.0
0.1
.01
.001
0
1
2
3
4
5
6
7
HOURS AFTER INJECTION

FIG. 2

MU-5724

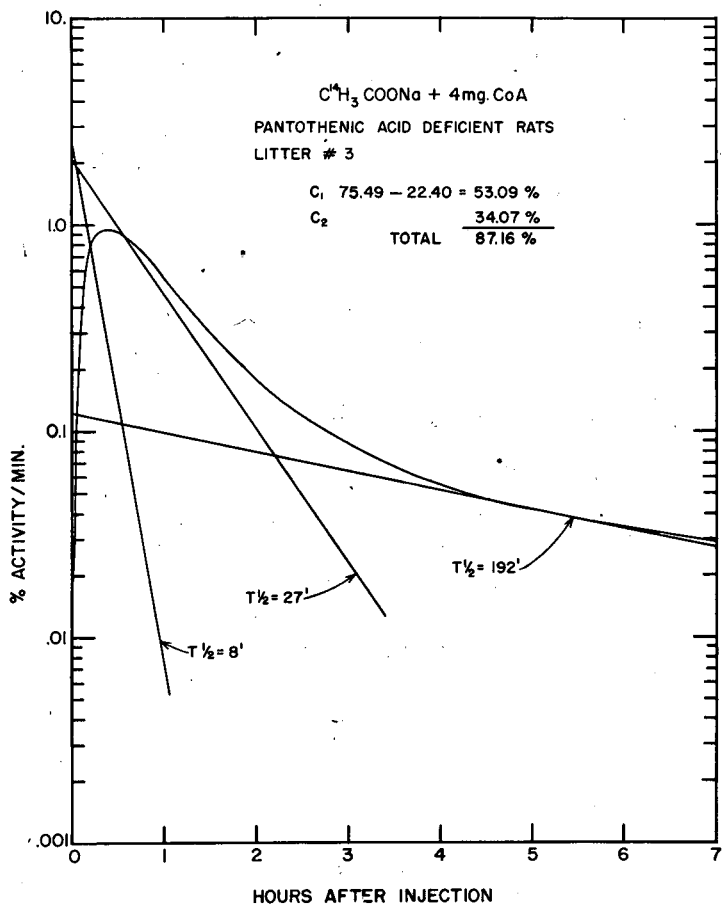
$C^{14}H_3COONa$ + 4mg. CoA
PANTOTHENIC ACID DEFICIENT RATS
LITTER # 3
C_1 75.49 – 22.40 = 53.09 %
C_2 34.07 %
TOTAL 87.16 %
T½ = 192'
T½ = 27'
T½ = 8'
% ACTIVITY/MIN.
10.
1.0
0.1
.01
.001
0
1
2
3
4
5
6
7
HOURS AFTER INJECTION

FIG. 3

MU – 5725

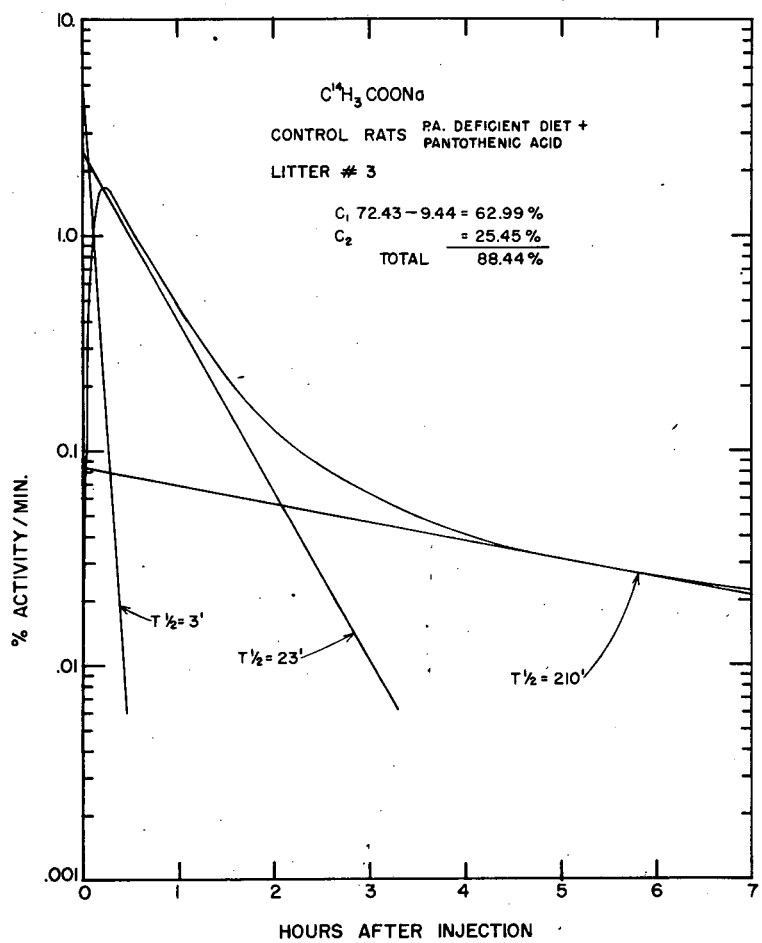
$C^{14}H_3COONa$
CONTROL RATS
P.A. DEFICIENT DIET + PANTOTHENIC ACID
LITTER # 3
C_1 72.43 − 9.44 = 62.99 %
C_2 = 25.45 %
TOTAL 88.44 %
T ½ = 3'
T ½ = 23'
T ½ = 210'
% ACTIVITY / MIN.
10.
1.0
0.1
.01
.001
0
1
2
3
4
5
6
7
HOURS AFTER INJECTION

FIG. 4

MU-5726

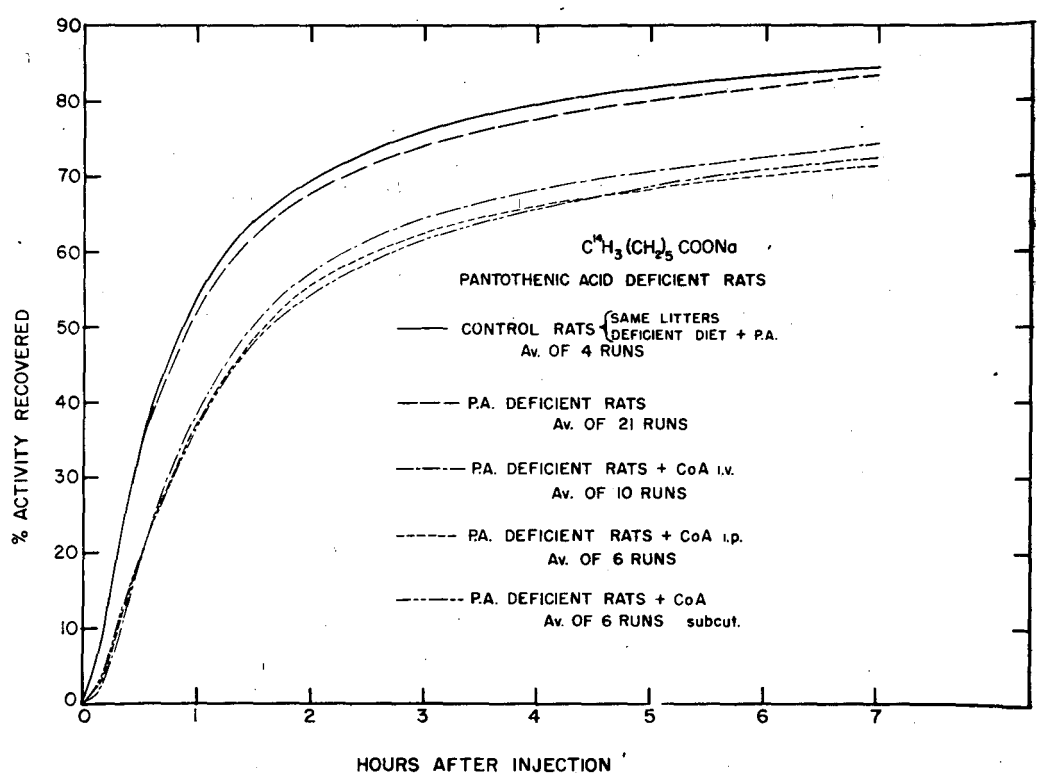
90
80
70
60
50
40
30
20
10
0
% ACTIVITY RECOVERED
0
1
2
3
4
5
6
7
HOURS AFTER INJECTION
$C^{14}H_3(CH_2)_5COONa$
PANTOTHENIC ACID DEFICIENT RATS
CONTROL RATS {SAME LITTERS DEFICIENT DIET + P.A.
Av. OF 4 RUNS
P.A. DEFICIENT RATS
Av. OF 21 RUNS
P.A. DEFICIENT RATS + CoA i.v.
Av. OF 10 RUNS
P.A. DEFICIENT RATS + CoA i.p.
Av. OF 6 RUNS
P.A. DEFICIENT RATS + CoA
Av. OF 6 RUNS subcut.

FIG. 5

MU - 5727

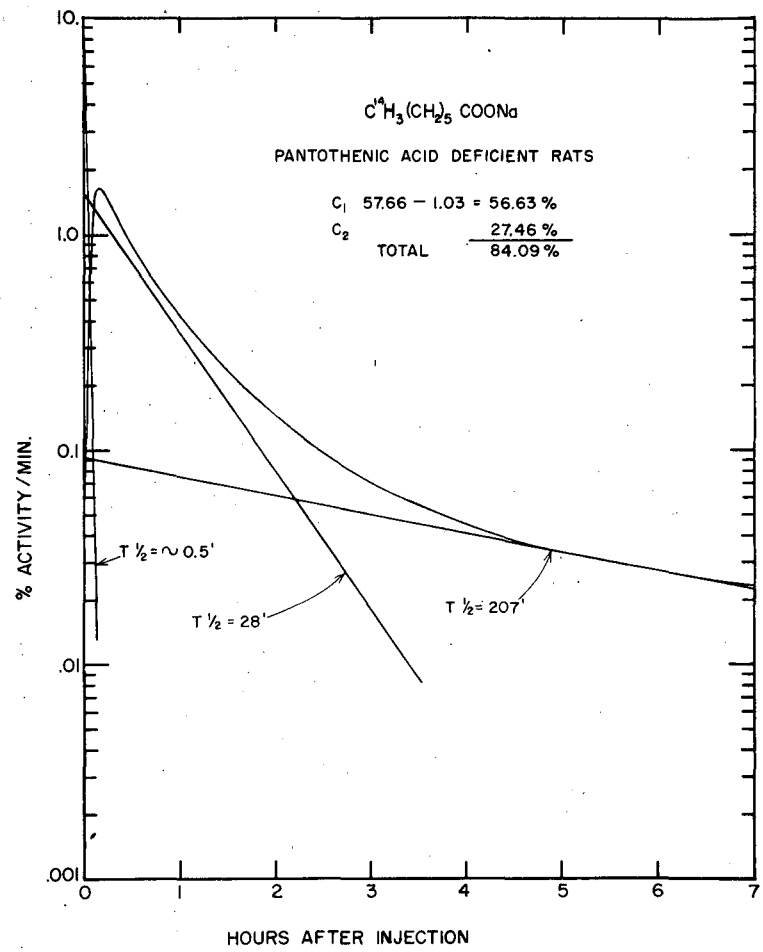
$C^{14}H_3(CH_2)_5$ COONa
PANTOTHENIC ACID DEFICIENT RATS
C_1 57.66 − 1.03 = 56.63 %
C_2 27.46 %
TOTAL 84.09 %
T ½ = ∼ 0.5'
T ½ = 28'
T ½ = 207'
% ACTIVITY / MIN.
10.
1.0
0.1
.01
.001
0
1
2
3
4
5
6
7
HOURS AFTER INJECTION

FIG. 6

MU − 5728

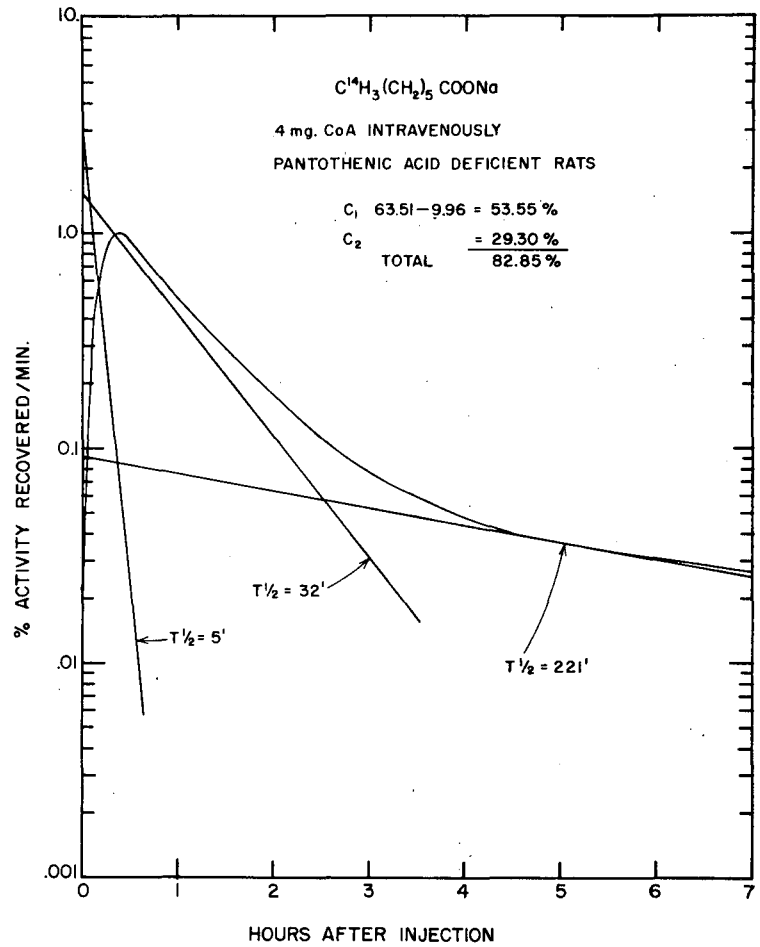
$C^{14}H_3(CH_2)_5$ COONa
4 mg. CoA INTRAVENOUSLY
PANTOTHENIC ACID DEFICIENT RATS
C_1 63.51 − 9.96 = 53.55 %
C_2 = 29.30 %
TOTAL 82.85 %
T½ = 32'
T½ = 5'
T½ = 221'
% ACTIVITY RECOVERED/MIN.
10.
1.0
0.1
.01
.001
0
1
2
3
4
5
6
7
HOURS AFTER INJECTION

FIG. 7

MU- 5729

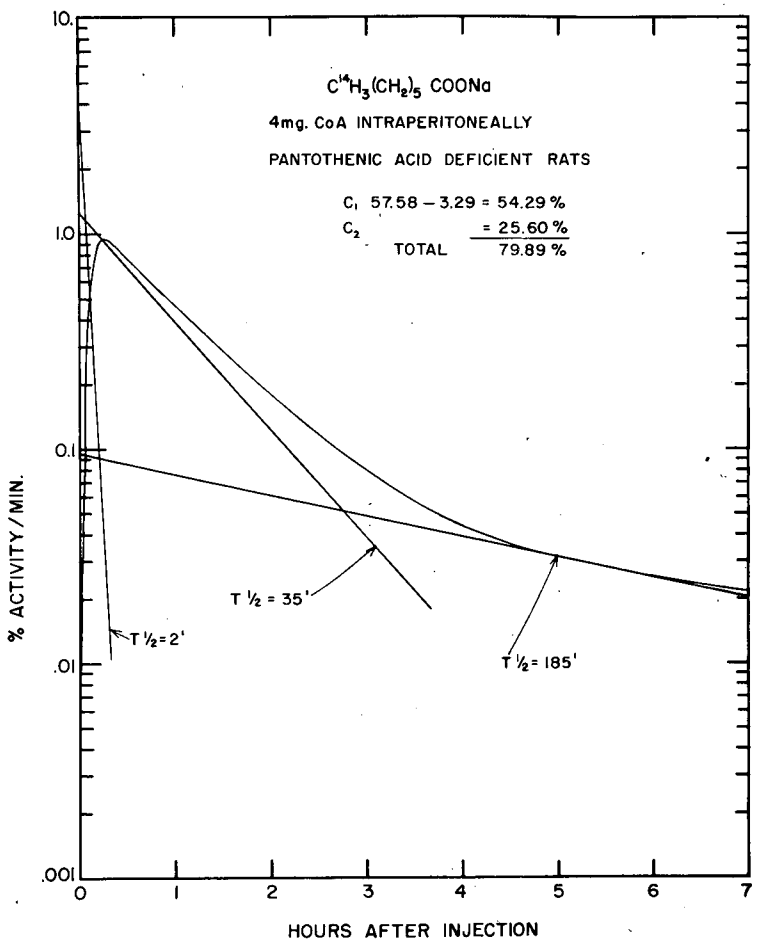
$C^{14}H_3(CH_2)_5$ COONa
4mg. CoA INTRAPERITONEALLY
PANTOTHENIC ACID DEFICIENT RATS
C_1 57.58 – 3.29 = 54.29 %
C_2 = 25.60 %
TOTAL 79.89 %
T ½ = 35'
T ½ = 2'
T ½ = 185'
% ACTIVITY / MIN.
10.
1.0
0.1
.01
.001
0
1
2
3
4
5
6
7
HOURS AFTER INJECTION

FIG. 8

MU – 5730

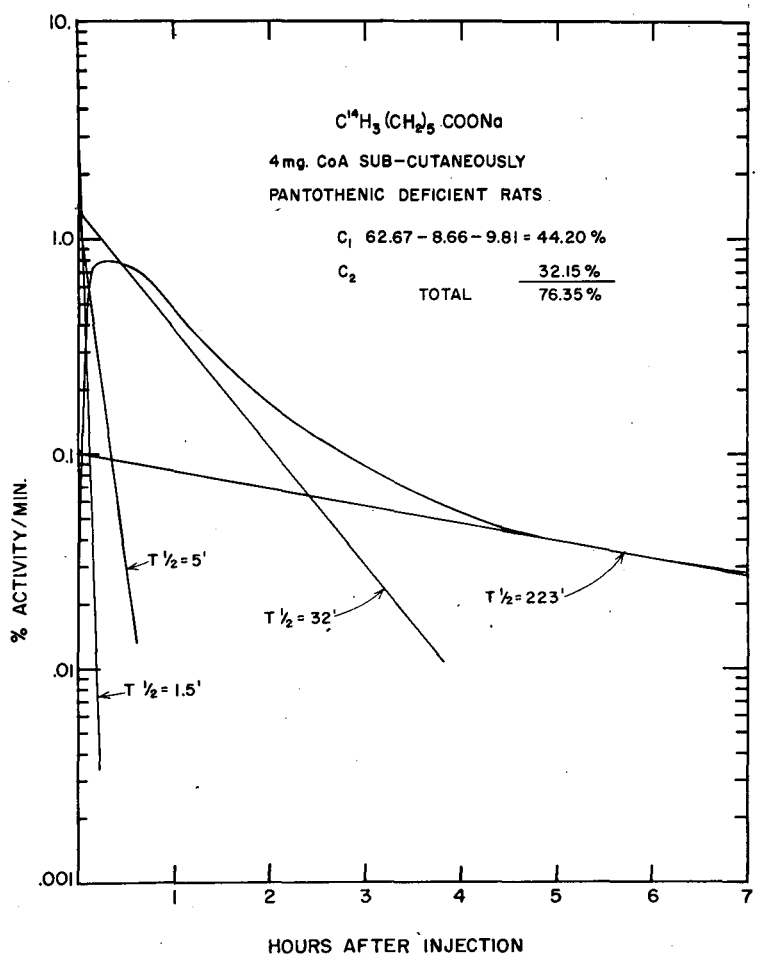
$C^{14}H_3(CH_2)_5$ COONa
4 mg. CoA SUB-CUTANEOUSLY
PANTOTHENIC DEFICIENT RATS
C_1 62.67 - 8.66 - 9.81 = 44.20 %
C_2 32.15 %
TOTAL 76.35 %
T ½ = 5'
T ½ = 32'
T ½ = 223'
T ½ = 1.5'
10.
1.0
0.1
.01
.001
% ACTIVITY/MIN.
1
2
3
4
5
6
7
HOURS AFTER INJECTION

FIG. 9

MU - 5731

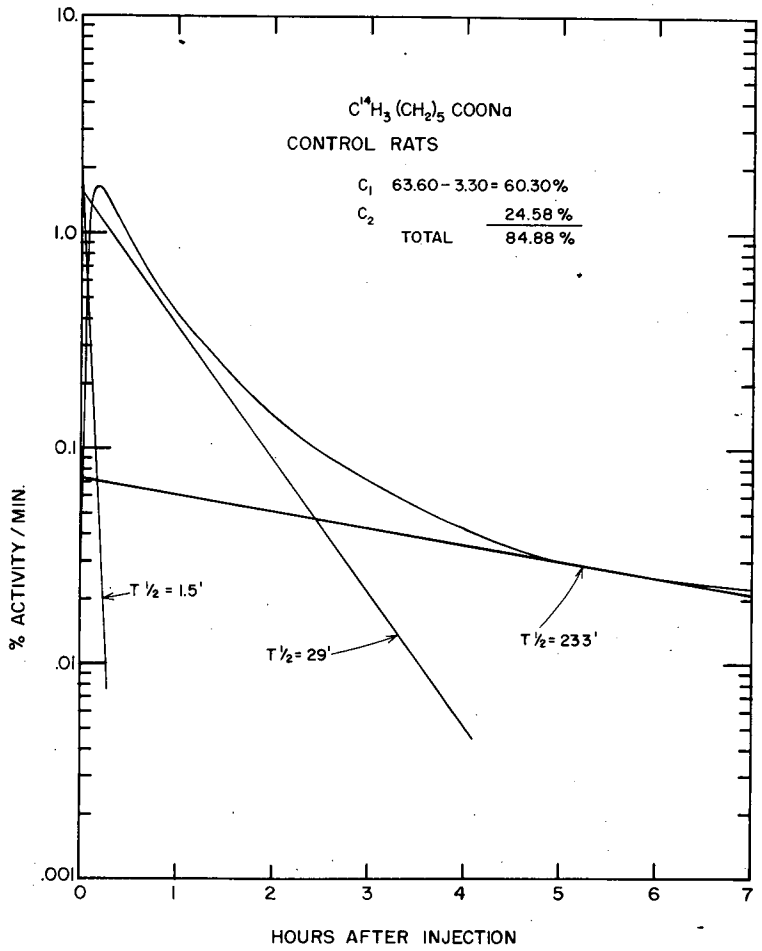

FIG. 10

MU - 5732

STUDIES ON ADENINE METABOLISM

E. L. Bennett and B. Krueckel

Turnover of Nucleotides and Nucleic Acids

Adenine is incorporated extensively and rapidly into the soluble nucleotides and the nucleic acids of C57 mice. The extensive incorporation of adenine-4, 6-C^{14} has made it possible to determine the turnover rates of the adenine of the 5-adenylic acid pool, the desoxynucleic acid (DNA) and the pentose nucleic acid (PNA) in various tissues of C57 mice after injection of adenine-C^{14}. Approximately 1.2 mg of adenine-C^{14} (approx. 15,000 dis/μg/min.) was injected intraperitoneally. Subsequently the mouse was sacrificed and the soluble nucleotides extracted with cold 10 percent trichloroacetic acid (TCA), the PNA separated by KOH treatment, and the DNA extracted by heating with 10 percent TCA. After suitable chromatographic separations, the specific activity of the 5-adenylic acid of the soluble nucleotides or the adenine of the nucleic acids has been determined with the aid of enzymatic spectrophotometric assay procedures.

The results of our first experiment to determine the half-life of both the DNA and the PNA in mouse tissues are shown in Table I. Further data may make the revision of some of the figures necessary. The data were obtained from one series of mice sacrificed up to 16 days after injection of adenine-C^{14}. The turnover rates or half-life of the various components are determined principally from the 3- or 7-day to 16-day data. In most cases, a component is indicated which is being turned over even more rapidly, but its half-life has not been determined as yet. Of particular interest are the relatively large incorporation of adenine into the DNA of the carcass (including the bone marrow) and intestines, and the rapid turnover of the DNA in these same tissues, as compared with the small incorporation of the adenine into the DNA of the liver and internal organs.

Effect of x-Irradiation on Incorporation of Adenine

Previous studies[1] have shown that x-irradiation greatly influences the amount of P^{32} incorporated into the DNA of various tissues when it is injected at times subsequent to irradiation. In general, the amount of P^{32} incorporated into the DNA is markedly decreased after irradiation, except in the small intestines, where a moderate decrease in the amount of P^{32} is noted at times up to 1 day after irradiation, followed by a large increase in P^{32} incorporation at 2 days. It was thought it would be of interest to study the effect of x-irradiation upon adenine incorporation, especially since the effect could be studied not only in the DNA fraction, but also in the PNA fraction and the soluble nucleotide fraction. The final data have been obtained for the DNA fraction only.

A-strain male mice were x-irradiated with 800 r (LD_{50}) under the conditions of the experiment. At subsequent time intervals, the animals were administered adenine-4, 6-C^{14} intraperitoneally. Two hours later, the animals were sacrificed and the tissues were fractionated. The specific activity of the DNA and PNA adenine and the 5-adenylic acid adenine was determined

1 L. Kelly and A. Payne, Fed. Proc. 12, 76 (1953).

after chromatographic separation. The results for DNA adenine are presented in Table II. These results are in agreement with the comparable values obtained after administration of P^{32}. In the carcass and internal organs there is a marked decrease, to about five percent, in the amount of adenine incorporated into DNA as compared to the nonirradiated control mouse. The small-intestine DNA shows an initial decrease in specific acitivity followed by an increase to two to three times that observed for the control mouse at 48 hours. The large intestine shows a similar pattern although the increase at 48 hours is not as large. In the case of adenine, the amount incorporated into the liver, stomach and kidney DNA is so small that significant values for the inhibition of incorporation by x-irradiation are difficult to obtain.

Analyses are also in progress to determine the effect of x-irradiation on the specific activity of the 5-adenylic acid and PNA-adenine.

Table I

Specific Activity and Half-Life of DNA and PNA Adenine and 5-Adenylic Acid in Various Tissues. (dix/min/μg Adenine).

Time After Injection	Liver			Carcass			Intestines		
	5-Adenylic Acid Adenine	PNA Adenine	DNA Adenine	5-Adenylic Acid Adenine	PNA Adenine	DNA Adenine	5-Adenylic Acid Adenine	PNA Adenine	DNA Adenine
2 hours	1550	130	10	405	133	105	3520	600	180
1 day	1510	400	14	265	188	195	1950	830	338
3 days	510	485	23	113	124	77	225	195	114
7 days	210	330	31	100	110	23	94	70	27
16 days	75	170	24	60	72	8.5	20	24	12.4
Half-life (days)	5.5	7	--	15	16	6	3.5	5.7	6

Time After Injection	Internal Organs			Stomach		
	5-Adenylic Acid Adenine	PNA Adenine	DNA Adenine	5-Adenylic Acid Adenine	PNA Adenine	DNA Adenine
2 hours	1100	58	21	2300	--	57
1 day	730	131	38	1140	--	180
3 days	260	130	32	355	--	140
7 days	220	125	42	220	--	39
16 days	123	80	40	100	--	21
Half-life (days)	8.5	14	--	7	--	10

Table II

Effect of x-Irradiation Upon the Incorporation of Adenine-C^{14} into the DNA of A-Strain Mice.

Time After x-irradiation* (Hours)	Tissue: Small Intestine s.a.**	Small Intestine % Normal	Lg. Intestine s.a.	Lg. Intestine % Normal	Carcass s.a.	Carcass % Normal	Int. Organs s.a.	Int. Organs % Normal	Stomach s.a.	Stomach % Normal	Liver s.a.	Liver % Normal	Kidney s.a.	Kidney % Normal
Control	119		103		132		40		40		--		--	
	185		141		134		51		75		5.1		3.6	
2 hours	92	77	50	48	31	24	17	42	--		--		--	
	131	71	47	33	56	42	16	31	31	42	3.2	43	< 1.0	< 28
6 hours	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	102	55	48	34	21	16	18	35	15	20	2.0	39	1.0	28
24 hours	113	95	69	67	8	6	4	10	14	35	--	--	--	--
	188	102	57	40	10.6	8	5.6	11	22	29	0.7	14	< 1.0	< 28
48 hours	396	332	140	136	5.3	4	2.2	5	31	78	--	--	--	--
	375	200	187	132	6.0	4	1.1	2	35	47	1.0	20	< 1.0	< 28

* The x-irradiation with 800 r (LD_{50}) required approximately 1 hour. The time is calculated from the end of the irradiation to the time of injection; 2 hours later the animals were sacrificed. Two separate series of experiments are represented by the above data.

** The specific activity (s.a.) is recorded in dis/min/μg of adenine in the isolated DNA. The adenine was isolated by chromatographic methods and the specific activity determined after hydrolysis of the DNA.

CONSTRUCTION OF A COBALT-60 GAMMA RAY SOURCE

R. M. Noller

In coöperation with the Health Chemistry Group of the Radiation Laboratory we have constructed a new γ-ray source which contains approximately 112 curies of Co^{60}. The source is so constructed that one may vary the dose rate over a considerable range by moving the Co^{60} slugs away from or toward the sample. The Co^{60} slugs are arranged in a ring around the sample. The size of this ring is continuously variable from a minimum diameter of 0.875 inches to a maximum diameter of 3.875 inches. The present sample holder is built so that it may hold a single sample in the center, or four individual samples arranged in a circle on a rotating table; with four samples in place, the minimum operating diameter is 1.750 inches. The sample containers are 1-ml volumetric flasks, each fitted with a glass tail for holding it in place.

In a previous quarterly report (June, July and August, 1952) we have described our use of the oxidation of ferrous ion and the reduction of ceric ion[1] for the quantitative determination of the dose rate from a 12-curie Co^{60} γ-ray source. The methods were in agreement with each other; $2.0^{+} \pm 0.2 \times 10^4$ rep/hr with the use of the ferrous ion actinometer and $2.2 \pm 0.4 \times 10^4$ rep/hr with the ceric ion actinometer. These values were in turn in agreement with a value of approximately $2 - 2.5 \times 10^4$ rep/hr as determined by air-ionization chamber measurements.

As before, the ceric sulfate solutions were made up in 0.8 N H_2SO_4 with water that had been re-distilled from alkaline permanganate. The glassware used had been cleaned in a dichromate cleaning solution and then rinsed six times with distilled water. The glassware was then further rinsed with six more portions of the specially distilled water. The change in concentration of ceric ion due to the effects of irradiation was measured in a Beckman spectrophotometer. The molar extinction coefficient of Ce^{+4} in 0.8 N H_2SO_4 is 5580 at 320 mμ[2] and the g value for ceric ions in acid solution is $3.\overline{3}$ ions per 100 e.v. Calculating on the basis of 93 ergs/ml/rep, it may be determined that the dosage received by an acid solution of ceric ions is expressed by the following equation:

$$\text{rep} = \Delta\,(5.63 \times 10^4)$$

where Δ = difference in optical densities of the irradiated and nonirradiated samples. The data for the actinometry of the Co^{60} γ-ray source are recorded in Table I. The accuracy of these values is probably not greater than about ± 10 percent. We have not tried determining flux density with any other source diameters because we have not as yet needed this information.

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1 T. J. Hardwick, Can. J. Chem. 30, 23 (1952).
2 Medalia and Byrne, Anal. Chem. 23, 453 (1951).

Table I

Standardization of Co^{60} γ-Ray Source

Sample Position	Diameter of Source (inches)	Irradiation Time (min.)	Approx. Conc. of Starting Solution (M/ml.)	Optical Density Observed	Optical Density Average	Optical Density Δ	Reps/Hr
Center	0.875	15	6.8×10^{-6}	0.745		0.028	3.15×10^5
"	"	10	"	0.751		0.022	3.71×10^5
"	"	20	"	0.718		0.055	4.64×10^5
---	---	0	"	0.781			
---	---	0	"	0.773	0.773		
---	---	0	"	0.766			
Center	0.875	30	6.8×10^{-6}	0.724		0.073	4.10×10^5
"	"	40	"	0.695		0.102	3.91×10^5
---	---	0	"	0.796	0.797		
---	---	0	"	0.798			
Center	1.750	30	3.4×10^{-7}	0.052		0.132	1.49×10^5
"	"	"	"	0.057		0.127	1.43×10^5
"	"	"	"	0.048		0.136	1.53×10^5
---	---	0	"	0.177			
---	---	0	"	0.188	0.184		
---	---	0	"	0.186			
All in source together in 4 tube holders	1.750	30	6.8×10^{-7}	0.108			
			"	0.110	0.1102	0.0696	1.57×10^5
			"	0.113			
			"	0.110			
---	---	0	"	0.180			
---	---	0	"	0.181	0.1798		
---	---	0	"	0.179			
---	---	0	"	0.179			

Table I
(continued)

Summary

Sample Position	Diameter of Source (inches)	Average Reps/Hr.
Center	0.875	3.9×10^5
"	1.750	1.5×10^5
4 Samples in 4 tube holders	1.750	1.6×10^5

EFFECTS OF HIGH-ENERGY RADIATION ON ORGANIC COMPOUNDS

R. M. Lemmon and R. M. Noller

The observations reported in our previous Quarterly Report on the radiation decomposition of some C^{14}-labeled compounds has led to increased interest in the effects of high-energy radiation on organic compounds. During the past quarter separate studies of the effects of high-energy β^-- and γ-irradiation on various compounds have been undertaken.

β^--Irradiation

Studies on the effects of high-energy beta particles have been carried out using a 3-5 Mev linear electron accelerator. This accelerator delivers 7-1/2 pulses per second, each pulse lasting 2 microseconds; the diameter of the beam is about 3 centimeters.

Since C^{14}-labeled choline chloride is so rapidly decomposed by its own radiation[1, 2] it was of interest to irradiate this compound with the electron beam. Unlabeled choline chloride (338 mg) and 0.1 mg of choline-N-methyl-C_1^{14} chloride (shown by paper chromatography to have a radiopurity greater than 99 percent were placed in a small flat-sided glass container which was afterwards evacuated. The walls of the container were each about 1 mm thick and the distance between the walls was approximately 2 mm. For the choline irradiation the electron beam was collimated to a diameter of 7 mm; in this way all of the beam emerging from the accelerator passed through the sample. The choline sample was held in the beam for 7 minutes, during which time it absorbed approximately 5×10^6 reps. A portion of the irradiated choline was chromatographed on paper (one-dimension) using a n-butanol:6 N HCl (2:1, by vol.) solvent. An x-ray film of the paper chromatogram showed the presence of two radioactive spots. One spot, containing 51 percent of the radioactivity, was identified as trimethylamine hydrochloride; the other spot, containing the remaining 49 percent of the total radioactivity, was unchanged choline chloride. In addition, a portion of the irradiated choline dissolved in water was added to a solution of 2,4-dinitrophenylhydrazine dissolved in dilute sulfuric acid. The resulting dinitrophenylhydrazone (which was completely inactive) was purified by silicic acid chromatography and identified as the acetaldehyde derivative by its melting point (146°).

The recent observation by W. J. Skraba, et al.[3] on the decomposition of C^{14}-labeled methanol led us to irradiate a methanol sample in the 3-5 Mev electron beam. To 20 cc of reagent-grade methanol was added about 700 μc of C^{14}-labeled methanol (in about 20 μliters). The methanol was dried and distilled directly into the irradiation vessel, which was a watch-shaped glass container with flat sides. The container was fitted at the top with a condenser (to return methanol boiled during the irradiation), at the upper end of which was fitted a round-bottom flask. The flask provided volume to prevent the building up of too much pressure in the system during the bombardment. In order to provide an oxygen-free, moisture-free atmosphere, the system was

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1 Quarterly Report for December, 1952, January and February, 1953.
2 J. Am. Chem. Soc. 75, 1867 (1953).
3 J. Am. Chem. Soc., in press.

partially evacuated, then filled with helium, and this process was repeated about 20 times. The methanol was then irradiated for 2-3/4 hours by the electron beam; during this time approximately 5×10^8 reps were absorbed by the alcohol. At the conclusion of the bombardment, unchanged methanol was distilled from the vessel, leaving behind a residual liquid which did not distill at 170° (atmospheric pressure). This residue weighed 851 mg, 5.9 percent by weight of the original methanol. The infrared spectrum showed that the residue was predominantly (approximately 90 percent) ethylene glycol. A one-dimensional paper chromatogram (butanol-ethanol-water solvent) showed the presence of labeled ethylene glycol, glycerol, and at least three other radioactive (and, at present, unidentified) spots.

Since ethylene glycol has been found to be the principal product of the beta-particle irradiation of methanol, an electron bombardment of ethylene glycol for 9-1/2 hours (giving over 10^9 reps) has also been carried out; however no data are as yet available on the products formed by this irradiation.

γ-Irradiation

Using the Co^{60} γ-ray source described in part 7 of this report, irradiations have been carried out on choline, acetyl choline, and various mixtures of pyrrole, pyrrole-α-aldehyde and benzaldehyde.

A sample of pure choline chloride was exposed in an evacuated glass tube to the γ-radiation of the Co^{60} source until 2.7×10^7 reps were absorbed. As a result of this irradiation 67 percent of the choline was destroyed; it thus appears that the γ-radiation is somewhat less effective for decomposing choline than is β^--radiation (in the self-decomposition of labeled choline, the compound was 63 percent decomposed by the absorption of 1.1×10^7 reps of energy). The irradiation with the γ-rays also resulted in the appearance of acetaldehyde and trimethylamine as the principal products. In addition, mass spectrography of the gases formed during the γ-irradiation showed that about equal molar quantities of methane and hydrogen were formed; these gases amounted to about 1.5 percent by weight of the original choline chloride.

A sample of 155 mg of analytically pure acetyl choline chloride and 8.3 mg (83 μc) of acetyl choline-N-methyl-C^{14} chloride (radiopurity shown by paper chromatography to be greater than 99 percent) was irradiated in the Co^{60} source for 13 days. During this time the sample absorbed 3×10^7 reps of energy. A portion of the irradiated sample was chromatographed on a paper strip (BuOH:6 N HCl, 2:1 by vol.). An x-ray film of this strip showed the presence of unchanged acetyl choline (96 percent of total radiopurity) and trimethylamine (4 percent). No other radioactive species was observed. The apparent great stability of acetyl choline toward radiation, contrasted with the corresponding instability of choline, is of considerable theoretical interest, particularly since these compounds are so important biologically. It should be mentioned here that we have observed the C^{14}-labeled acetyl choline is vastly more stable towards its own radiation (approx. 1 percent decomposition by 10^7 reps) than is choline (63 percent decomposition by 10^7 reps).

Of particular interest has been the possible formation of porphyrins from simpler substances under the influence of ionizing radiation. In order to study this possibility, pyrrole-α-aldehyde, pyrrole, and benzaldehyde mixtures,

and various amino acids have been subjected to γ-irradiation. At present, analytical methods are being developed in order to determine the products of these irradiations.

The data so far gathered for the β^-- and γ-irradiations are summarized in Table I.

Table I

Compound Irradiated	Type and Energy of Radiation	Energy Absorbed Reps	Observed % Change to Other Chemical Species	Radiation Products Identified
Choline Chloride	3-5 Mev β^-	5×10^6	51	Trimethylamine Acetaldehyde
Choline Chloride	1.1 Mev γ	2.7×10^7	67	Trimethylamine Acetaldehyde Methane Hydrogen
Acetyl Choline Chloride	1.1 Mev γ	2.4×10^7	4	Trimethylamine
Methanol	3-5 Mev β^-	5×10^8	6	Ethylene Glycol Glycerol
Ethylene Glycol	3-5 Mev β^-	1.5×10^9	--	---

GENERAL CHEMISTRY

W. M. Latimer, Director

METALS AND HIGH-TEMPERATURE THERMODYNAMICS

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

HEATS OF FORMATION AND ABSOLUTE ABSORPTION COEFFICIENTS OF HIGH-TEMPERATURE MOLECULES

A new King furnace is almost completed. Plans are being worked out for its use to determine the absolute absorption coefficients and heats of formation of important high-temperature molecules.

REFLECTION COEFFICIENTS OF MOLECULAR BEAMS

Apparatus is under construction for the measurement of the reflection of molecular beams from solid surface and the determination of the important variables that control reflection.

MAGNESIUM OXIDE GAS

Study of the MgO spectrum in absorption and emission has confirmed early measurements that indicated that the generally accepted $^1\Sigma$ ground state of MgO is higher in energy than a triplet state that is the true ground state. Thus MgO gas is more stable than previously believed on the basis of the old assignment of the ground state.

REFRACTORY SILICIDES

Work on the ternary diagrams of systems containing Si, C, and refractory metals or Si, N, and refractory metals has been essentially completed and the regions of stability of the various phases determined.

SODIUM CARBONATE VAPOR

Work is still in progress on the study of Na_2CO_3 vapor. Results to date indicate that Na_2CO_3 forms a constant-boiling liquid composition close to Na_2CO_3 in composition. This constant-boiling liquid is in equilibrium with Na(g), O_2(g), and CO_2(g).

HIGH-TEMPERATURE HALIDE MOLECULES

The study of CF and CF_2 has been essentially completed. Work is still in progress on the study of the effect of water on the volatility of molybdenum chlorides.

BASIC CHEMISTRY, INCLUDING METAL CHELATES

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

STUDIES INVOLVING AMMONIA

A program has been initiated involving the preparation of a variety of metal amides. These amides will be examined by x-ray diffraction methods in an attempt to determine their structures, and the decomposition pressures will be measured. Thus far, $LiNH_2$, $NaNH_2$, KNH_2 and $Ni(NH_2)_2 \cdot 2NH_3$ have been prepared and submitted for x-ray examination. A rough determination has been made of the vapor pressure of $LiNH_2$ at 370° and of the decomposition pressure of NH_3 over Li_2NH and $LiNH_2$ at 250°. These compounds are attacked by oxygen and moisture and they must be handled in an inert atmosphere. A suitable argon dry-box has been set up for handling these and similar compounds.

Both $LiBH_4$ and $NaBH_4$ appear to form ammonates and the formulas and dissociation pressures of these compounds are being determined.

A helium gas-displacement densitometer has been set up for measuring the densities of solids whose densities cannot be obtained by the usual pycknometric methods. The apparatus apparently yields densities accurate to 0.5 percent, and will be useful for determining the densities of amides and hydrides.

A solution of beryllium chloride in NH_3 and a solution of beryllium bromide in NH_3 have been electrolyzed in a cell with a sintered glass partition between the electrode compartments. Deep blue solutions of beryllium ($Be^{+++} + e_2^{=}$) were obtained in the cathode compartment in each case. Apparently this is the first report of the existence of a solution of beryllium in ammonia.

THERMODYNAMICS OF INDIUM

This project has been completed and the results have been published in UCRL-2202.

COMPLEXING OF SCANDIUM BY FLUORIDE ION

The equilibrium constant for the reaction

$$Sc^{+++} + HF = ScF^{++} + H^{+}$$

is being measured by the method previously used for similar work on indium.

THERMODYNAMICS OF THIOSULFATE

Equilibrium tubes for approaching equilibrium in reaction (A) from both sides and at various ionic strengths are about ready for analysis.

$$\text{(A)} \quad S_2O_3^{=} + 2Ag = SO_3^{=} + Ag_2S$$

One set has been in an oil bath at 123° and another set on a shaker in a 25° water bath. An additional set has been prepared and will be put in the oil bath at about 200° when it is empty. An attempt was made to measure some aqueous heat capacities, but the calorimeter at hand proved unsuitable. Experiments have been conducted to find an oxidizing agent capable of oxidizing $S_2O_3^{=}$ to $SO_4^{=}$ in a reaction for calorimetry. The following are apparently unsatisfactory: acid ceric, acid iodate, basic iodate. Acid bromine shows some promise and will be tried. A hygrostat method is being pursued for the preparation of stoichiometric $Na_2S_2O_3 \cdot 5H_2O$ crystals suitable for the calorimetric study.

STUDY OF HYDRATES

The most satisfactory method of preparation of $CaCl_2 \cdot 2H_2O$ has proved to be the vacuum line technique described in UCRL-2179. Two more runs have been made on its heat of solution in water, giving the value 10.50 ± 0.02 kcal./mole; the conclusions from this work will be summarized in the September quarterly report.

RARE EARTH FLUORIDE COMPLEX IONS

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

FERRIC FLUORIDE COMPLEX IONS

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

HYDROLYTIC POLYMERIZATION OF ZIRCONIUM

This project has been completed and the results will be published shortly as a UCRL report.

CHEMICAL ENGINEERING (PROCESS CHEMISTRY)

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

PREPARATION OF TITANIUM METAL

A. W. Peterson and L. A. Bromley

Film boiling has been attained with titanium iodide at a pressure of approximately 10 mm Hg. It was readily ascertained that film boiling occurs, by the simultaneous drop in current and increase in potential drop across the hot filament at high heat fluxes.

Because of the film boiling, a deposit has been obtained on the filament. However, this deposit was not metallic titanium as desired. It is thought that impurities in either the vapor or liquid phase may have caused this undesirable deposit.

In order to eliminate these impurities, a high vacuum and simple distillation apparatus has been designed and constructed. Film boiling will be tried in pure titanium iodide. The high vacuum degassing will remove any gaseous impurities (as oxygen, nitrogen). The simple distillation will remove solid impurities (as titanium oxides, nitrides). The vapors from the distillation will be run through a bed of hot metallic titanium to remove free iodine.

FILM BOILING FROM SUBCOOLED LIQUIDS

. E. I. Motte and L. A. Bromley

Runs are now in progress using ethyl alcohol and the smallest diameter heating element. It has been found that owing to limitations of the equipment the maximum amount of subcooling attainable is approximately 100°F at low velocities (3 ft/sec) and 40°F at high velocities (15 ft/sec) of the fluid. The mechanical seal in the small transfer pump has been replaced and the mechanical seal of the large centrifugal pump is now being replaced. Preparations have been made to test the effect of turbulence. Turbulence will be produced by various sized screens located above the nozzle below the heating element.

THERMAL CONDUCTIVITY OF GASES AT HIGH TEMPERATURES

A. J. Rothman and L. A. Bromley

The thermal conductivity apparatus has been completed and the resistance thermometer repaired.

About 43 runs have been completed, and measurements have been made on air and nitrogen at 50°C, and on a number of gases at 360°C and some at 560°C. Gases used at the higher temperatures were nitrogen, carbon dioxide,

argon, and mixtures of N_2 and CO_2. The results compare favorably with literature values available, but are several percent below Keyes's data for these gases.

A burnout of the emitter heater leads has necessitated shutting down the equipment. When repairs are completed, further high temperature runs will be made.

Use tests indicate that stainless steel and titanium are unsatisfactory materials for stirring molten tin at 500°C. Molybdenum is to be tested next.

AGITATION OF LIQUID-LIQUID SYSTEMS

L. Fick and T. Vermeulen

Studies are being continued for the purpose of obtaining a general correlation of drop size in emulsions versus liquid properties, paddle geometry, and mixing speed. The liquid systems studied up to the present time divide into two categories. One set, which fits a generalized correlation, comprises those systems which take a measurable time to reach the steady-state drop size, indicating slow breakup and correspondingly slow coalescence. The second set comes to steady state too quickly for rate measurement, indicating fast breakup and rapid coalescence both in the high-turbulence and low-turbulence regions of the mixing tank. Such systems show larger drop size than the first set.

SOLUBILITY STUDIES

M. Cook and D. N. Hanson

The air-bath thermostat mentioned in UCRL-2179 Supp. has been constructed and preliminary tests are in progress. From these tests it appears that with some small modifications the working area in the thermostat will provide temperature control at -35°C to ± 0.01°C at any given point, while the inlet and outlet temperature of the recirculating air will differ by 0.1 - 0.2°C.

The resumption of experiments as described in UCRL-2179 Supp. will begin on about June 15 and it is expected that the data will be completed in the range from -35°C to +45°C by July 15.

THERMAL DIFFUSION IN LIQUIDS

J. Powers and C. R. Wilke

Equipment has been designed for measuring the soret coefficient in a modified glass-diaphragm diffusion cell. A batch parallel-plate apparatus has also been designed to investigate the batch thermogravitational method. Further modifications have been made on the pilot plant scale thermogravitational equipment.

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CAPACITY OF PERFORATED-PLATE LIQUID-VAPOR CONTACTING COLUMNS

C. D. Hunt, D. N. Hanson, and C. R. Wilke

Experimental data on pressure drop, entrainment and dumping are being examined in an effort to obtain a general correlation for perforated-plate distillation columns.

Photographic studies of column operations are in progress to establish the nature of the flow more definitely as a basis for theoretical interpretation of pressure drop and entrainment.

GAS-PHASE MASS TRANSFER STUDIES

E. J. Lynch and C. R. Wilke

Psychrometric data for water vapor-air have been obtained for film pressure factors, p_f, as low as 0.69 atm. The data indicate that the group

$$\frac{k_g p_f M}{h}$$

is nearly independent of gas, humidity and flow rate. Additional data are being taken to verify this conclusion.

Construction of equipment is under way for gas-phase mass transfer studies in fixed beds in absence of liquid flow. An existing 24-inch absorption tower is being prepared to extend previous work (UCRL-2057 Rev.) to large-size packings.

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