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PROGRESS REPORT
CHEMISTRY SECTION

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Contract No. W-7405-eng-48 & 48B

PROGRESS REPORT FOR OCTOBER, 1947

CHEMISTRY SECTION

I. Perlman, R. F. Leininger,
B. Tolbert, & W. M. Latimer

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UNIVERSITY OF CALIFORNIA RADIATION LABORATORY

PROGRESS REPORT FOR OCTOBER, 1947. CHEMISTRY SECTION

PART A. REPORTED BY I. PERLMAN

Contract No. W-7405-eng-48

Nuclear Reactions with High Energy Particles

Irradiation of Antimony with 200 Mev Deuterons

A new 4-day tellurium activity has been found which is the parent of a new 40-hour antimony. Critical x-ray absorption measurements showed that the antimony decays by K-capture. The tellurium parent (Te^{118}?) of the 3.4-minute antimony positron-emitter has a half-life of about 6 days.

Relative yield determinations for the different spallation reactions are being made. There is a general trend downward in yield as one departs from the target element in comparing product nuclei that are similarly situated with respect to their stable isotopes. The relative yields that have so far been obtained may be listed as follows: Te 1-2, Sn 0.2, In 1.0, Ag 0.3, Pd 10^{-3}, Ru 10^{-4}, Mo 10^{-4}, Y 10^{-5}. For a given mass number there may be sharp differences in yield between isobars. For example, Cd^{109} is formed in 100-fold greater yield than Pd^{109}. Similarly, In^{112} and Ag^{112} are formed in approximately equal yields while Pd^{112} is formed in much lower yield. Apparently some mechanisms for energy dissipation in the highly excited nuclei are favored over others but no generalizations can yet be made. It is worth pointing out however than in one of the examples given above Cd^{109} can be reached by a great many different mechanisms, whereas the mechanisms for

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the formation of Pd^{109} are more restricted and probably involve the ejection of a particular number of charged particles.

Irradiation of Arsenic with 200 Mev Deuterons

In the bombardment of arsenic with 200 Mev deuterons there are some chemical fractions which had not previously been investigated. A new 36-hour activity has been found in the chromium fraction while in the zinc fraction the 57-minute β^--emitter and 14-hour isomeric transition isomers of Zn^{69} have been found. In the nickel fraction the 2.6-hour Ni^{65} and the 58-hour Ni^{66} have been confirmed.

Relative yields have been determined for the different chemical fractions in this irradiation and these are as follows:
Se 0.02; As 1; Cu 0.1 - 1.0; Ni, Co and Fe 0.005.

Irradiation of Copper with 200 Mev Deuterons

When copper is irradiated with 200 Mev deuterons there is a fairly smooth drop in yield in elements from copper to chlorine. If copper is assigned the arbitrary yield of unity, the zinc fraction shows a relative yield of 0.04 and the chlorine of 0.001.

Chemistry and Structure of Actinide Elements

Separation of Lanthanides and Actinides by Elution with Fluosilicate from an Adsorption Column

Using Nalcite resin as an adsorbing medium and citrate ion as the elution agent, it has been found possible in the past to effect good separations of certain adjoining rare earths or actinide elements, but that there will be a particular lanthanide element that will be poorly separated from a particular actinide element. For example element 61 and americium cannot be separated readily by citric acid elution. However, using 0.2 M ammonium fluosilicate, $(NH_4)_2SiF_6$, at pH 2.7 it was possible to completely separate americium from element 61 in a single pass through a column only 1.5 cm. long using a flow rate of .3 ml. per minute per cm^2. Curium was also present in the experiment and a moderately good separation of americium and curium resulted. The three elements came off the column in the order element 61, curium, americium.

Solubilities of Actinides and Lanthanides at Low HF Concentrations

It has been suggested that the function of fluosilicate ion in the precipitation and adsorption-elution methods of separating lanthanide from actinide elements is to serve as a buffered source of very low concentrations of fluoride ion. To explain the results on this basis it is necessary to assume that lanthanide ions tend to form stronger complex ions with fluoride at all stages, that is, the mono-, di, and trifluorides. The column elution experiment mentioned above can then be explained by assuming that element 61 forms a mono- or difluoro complex ion more readily than do americium and curium. Similarly, the precipitation of lanthanide elements with fluosilicate leaving actinide elements in solution can be explained by assuming that the lanthanide elements alone can reach the insoluble trifluoride state at the fluoride concentrations available. To test these ideas a macroscopic amount of lanthanum with element 61 and americium tracers was treated with very low concentrations of HF such that precipitation of the lanthanum was incomplete. It was found that when only 30% of the americium had precipitated, over 90% of the element 61 had left solution, tending to confirm the assumed greater affinity of the lanthanide element for the available fluoride ions.

Crystal Structure of Samarium Oxychloride

The compound SmOCl has been prepared and found to have a tetragonal structure with cell constants a = 3.97 ±0.005 and

$c = 6.692 \pm 0.010$. This compound is isomorphous with PuOCl and cell constants are approximately 1% below those of PuOCl. This checks the fact that the cell constants for SmF_3 are also less than those of PuF_3 by approximately 1%.

PART B. REPORTED BY R. F. LEININGER

Studies of Astatine

In order to compare At with I it was felt necessary to do some experiments on the latter substance in "carrier free" samples. Extraction experiments on tracer I_2 were attempted and coefficients as large as thirty were obtained upon repeated extraction. The extraction appeared to be independent of extraction time. The addition of Br_2 caused a gradual removal of I_2 from the $C\,Cl_4$ layer that was 15 percent complete in three days. Sulfite rapidly removed about 20 percent of the remaining I_2 left after extracting with water four times. Subsequent treatment with sulfite failed to remove any appreciable amount of iodine. Dr. Hamilton suggested on the basis of some earlier work done with tracer I_2 that the non-extractable iodine had exchanged with chlorine in the $C\,Cl_4$.

Carrier free iodine in $C\,Cl_4$ solution was placed in a tube containing foils of six different metals that had previously been cleaned at elevated temperatures in hydrogen. The tube was then evacuated, sealed off, and then heated to 300° C for one-half hour. Subsequent examination of the metal foils yielded the following results.

Metal	Percent I_2 (10/23/47)	Percent I_2 (3/14/47)	Percent At (3/11/47)
Al	0.3	0	.17
Ni	1.3	0	.64
Au	.9	0	.12
Pt	3	1	34.0
Cu	37	50	.57
Ag	57	49	65.0

Thus there seems to be a correspondence between astatine and iodine in all cases except platinum and copper.

Additional experiments on the carrying of astatine by silver iodate were attempted. However the results of these were too inconclusive to be reported at this time. The -1 state was investigated more closely and found to carry on Ag I after reduction with $Fe\ SO_4$. Distillation of a sulfuric acid solution of astatine containing $Fe\ SO_4$ caused 70 percent of the activity to appear in the first 20 percent of the distillate.

Ionic migration experiments have been continued in astatine. Since a basic solution permitted migration and an acid solution prevented it in both cases of positive oxidation state, an attempt in being made to determine the ionization constant of these weak acids. In the general acid $HA \rightleftarrows H^+ + A^-$ the ratio A^-/HA depends only on the pH and the equilibrium constant through the relationship $\frac{(A^-)}{(HA)} = \frac{K_A}{(H^+)}$. migration experiments in buffered solution should seem to determine approximately the constant of ionization of these weak acids of astatine. So far a tentative value of $K=10^{-7}$ has been assigned to the lowest positive oxidation state thus far prepared. This ion is formed by dissolving astatine in concentrated HNO_3. Since the ionization constants for the halogen acids H ClO, H Br O, and HIO are $5.6x10^{-8}$, $2x10^{-9}$, $\sim 10^{-11}$ respectively, one would expect HAtO to be very weak acid with $K= < 10^{-11}$. At the present time the best assignment for this oxidation state appears to be $HAtO_3$.

PART C. BIO-ORGANIC CHEMISTRY

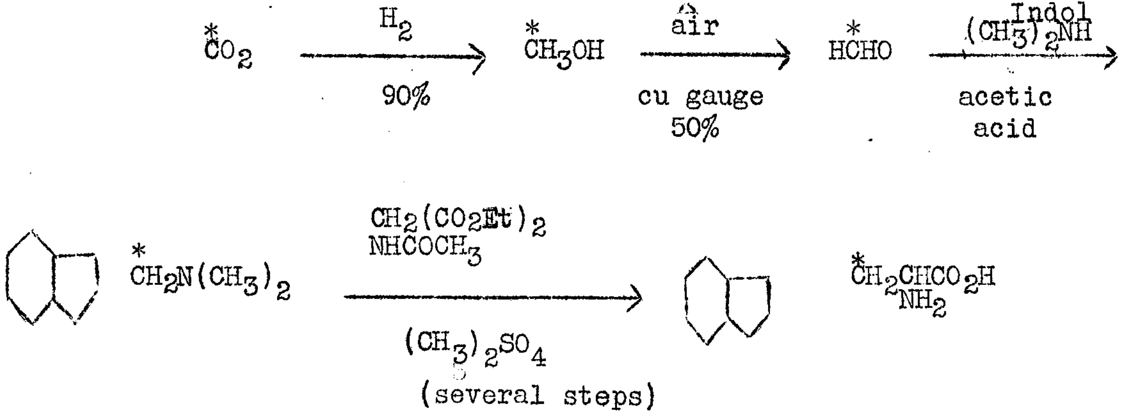
REPORTED BY B. TOLBERT

Synthetic and Experimental Organic Chemistry.

A book on isotopic carbon is being written by five members of the Synthetic Organic Group (Calvin, Heidelberger, Reid, Tolbert and Yankwich) which is to be published by John Wiley and Sons. The book will appear sometime in 1948. The book, designed as an advanced laboratory manual on isotopic carbon, deals with this subject in all its phases from a review of the experimental applications to a detailed discussion of measurements of isotopic concentrations, published syntheses of labeled compounds (both chemical and biological), and degradation methods.

The synthesis of ring-labeled (1,3,5-carbon fourteen) toluene has been completed and a report is being written which will be issued shortly. The specific activity of the product produced at this time is only moderately high for the material from this run will be used for chemical experiments and to determine distribution of radioactive atoms. The mechanism postulated for the reaction (see Progress Report for August, 1947) has been found to agree with the activities of the radioactive intermediate compounds and by-products isolated in the synthesis. The toluene itself has not yet been degraded.

The synthesis of radioactive dl-tryptophane labelled in the side chain on the β atom has been completed by the following series of reactions.



$$\overset{*}{C}O_2 \xrightarrow[90\%]{H_2} \overset{*}{C}H_3OH \xrightarrow[\text{cu gauge } 50\%]{\text{air}} H\overset{*}{C}HO \xrightarrow[\text{acetic acid}]{\text{Indol } (CH_3)_2NH}$$

The overall yield of the tryptophane is about 10 percent based on the carbon dioxide used. It is planned to synthesize α-labeled 3-indol acetic acid from the condensation products of the formaldehyde with indol. This compound will be condensed with KCN to form the nitrile which will then be hydrolyzed to give the acetic acid derivative. This compound is of considerable interest as a plant growth hormone and projected experiments are planned with the Agriculture Department of the University.

A rapid method of combustion or burning of organic substances to carbon dioxide for radioactivity measurements has been developed using a sodium peroxide bomb method (Paar-Micro Peroxide Fusion Bomb). Less than an hour is required using this method for the conversion of an organic sample to dry weighed barium carbonate. The carbon recovery is 100 percent within the limits error of the experiment; reproducibility is within 1 percent.

Experiments to determine the rapidity with which barium carbonate on plates exchanges with carbon dioxide of the atmosphere is being studied. Experiments are being carried out to determine the conditions for and rate of exchange in various carbon dioxide atmospheres. These experiments are of interest and are necessary when assay procedures using counting of solid barium carbonate samples are utilized.

Propylene labeled at least 98 percent on the methyl carbon has been synthesized by decomposition of n-propyltrimethylammonium hydroxide.

$$CH_3CH_2\overset{*}{C}H_2Br \xrightarrow{(CH_3)_3N} CH_3CH_2\overset{*}{C}H_2\text{-}N(CH_3)_3Br \xrightarrow{Ag_2O}$$

$$CH_3CH_2CH_2N(CH_3)_3OH \xrightarrow[\text{to dryness}]{\text{heat}} CH_3CH \quad \overset{*}{C}H_2$$

This synthesis is to be compared with dehydration of propyl alcohol over either phosphoric acid or alumina where 50-50 equilibrium mixtures of propylene with regard to isomerization of the double bond.

Biological Chemistry.

The biological conversion to nicotinic acid of dl-tryptophane, synthesized as mentioned in the previous section, will be studied. Joint experiments with the Poultry Husbandry and Home Economics Departments of the University of California are planned using rabbits and rats as the experimental subjects. The resolution of tryptophane will be undertaken in connection with these experiments.

Dopa (dihydroxyphenylalanine) whose synthesis was outlined in last month's report has been administered to three mice bearing melanoma sarcomas. Investigation of the distribution of the carbon activity in the tissues of the mice is underway. The information available to date indicates that most of the Dopa is excreted with relatively no accumulation in the body tissues. No marked organic localization has been noted thus far.

The experiments on the metabolism of dibenzanthracene in mice is being continued and more information accumulated with respect to the occurrence in the animals of water soluble metabolites from the dibenzanthracene.

Photosynthetic Chemistry.

In the studies of photosynthesis, it is of considerable interest to isolate the maximum yield of intermediates from the fixation of carbon dioxide by various plant materials. Studies are therefore being undertaken on the relationship of prehistory to the dark fixation of algae with respect to the growth and fixation powers. It has been found that if algae are illuminated for one hour prior to feeding of radioactive carbon dioxide in the dark, over ten times as much radiocarbon dioxide is fixed as if the illumination were not done. Using these techniques the plants have been shown to absorb more carbon dioxide then has previously been reported in the literature. The rate and growth of carbon dioxide fixation with illumination and the rate of decay of this reducing power on turning off the light is being determined.

A carbon dioxide analyzer has been built by the Electronics Department for use in photosynthesis experiments and is now being tested. It works on the principle of total absorption of infra-red radiation following partial absorption of radiation by a standard or unknown sample of carbon dioxide. Interrupted infra-red radiation from two short Globar heaters is passed alternately through a standard and unknown cell. The residual radiation from each cell is picked up by two carbon dioxide-filled acoustic resonators (the heat from the radiation causes the gas to expand or contract producing a mechanical effect). Microphones in these resonant cells pick up signals whose intensities are a function of the carbon dioxide content in the unknown and standard cell. These signals are then amplified and recorded on a balancing potentionmeter.

Separation of the radioactive amino acids on ion exchange resins is being studied. The amino acids include alanine, which is in biological equilibrium with pyruvic acid, glycine, aspartic acid and glutamic acid. Alanine has been degraded and the radio carbon in the 3-position determined.

The work on the role of phosphorus in photosynthesis has been resumed and further studies are being made using radioactive phosphorus.

PART D. REPORTED BY W.M.LATIMER

(Project 48B, W.M.Latimer, Director)

Metals and High Temperature Thermodynamics

Gaseous Species at High Temperatures

Work is in progress for the determination of the heats of formation of CN and CuCl by emission and absorption spectra, respectively. The CN work will also give the relative absorption coefficients of CN and C_2.

Uranium Halide Phase Diagram.

A new apparatus for determining cooling curves for use in induction heating is being devised.

Refractories. The fabrication of TiC, ZrC, CbC, and TaC parts are being worked out by a process starting with graphite and the metal halides. If successful, this method will make this material much more readily available.

Liquid Metal Systems.

X-ray patterns which have been taken of samples in the NaBi, UBi_2, Bi phase region of the ternary system which indicate that no ternary compounds are formed. Cooling curves are to be run next to obtain the characteristics of the ternary diagram. Analytic procedures have been worked out for Na-Sn systems in preparation for the study of the heats of formation of the intermetallic compounds.

Thermodynamic Reports.

A report on the thermodynamic properties of the uranium compounds and one on the thermodynamic properties of the neptunium compounds have been completed. A similar report on plutonium is almost completed. A paper on the vapor pressure of graphite has been completed.

Basic Chemistry

Ether Extraction of $UO_2(NO_3)_2$ (Preparation of Anhydrous Salt).

A sample of $UO_2(NO_3)_2 \cdot 6H_2O$ was ground in a mortar and placed in a dessicator over $CaCl_2$ at reduced pressure (from 30-60 mm Hg) for several weeks. An analysis showed 3.05 mols H_2O and 1.78 mols (NO_3) per mol of uranium. A sample of this partially dehydrated salt was placed under a vacuum of 1×10^{-4} to 8×10^{-5} mm Hg for about 72 hours. An analysis showed 0.02 mols H_2O and 1.15 mols $(NO_3)^-$ per mol of uranium.

Absorption Spectra.

Measurements of the absorption spectrum of the dehydrated, partially decomposed salt dissolved in anhydrous ether were made to determine if the addition of water would bring about the formation of new species. Small changes occurred indicating such species. However, the results were observed by changes in the absorption that occurred between measurements in which no water was added. As compared to the increase in absorption which occurs immediately when such a solution is exposed to light, these measurements showed a decrease during several hours of standing and then an increase. It is believed the increase is explainable by the formation of a precipitate produced by a light reaction, that is at first colloidal and then precipitates out on the walls of the cell.

Conductivity.

The conductivity of the ether solution of salt containing 3.05 mols H_2O and 1.78 mols $(NO_3)^-$ per mol of uranium was measured. A solution 6.4×10^{-3} M in uranium had a specific conductance of ca. 1.24×10^{-7} mols. Therefore it is concluded that the salt is essentially ionized in ether solution.

The Extraction of Zr (IV) by TTA.

It was stated previously that the distribution of Zr (IV) between dilute aqueous perchloric acid solution and benzene TTA solution was found to be dependent on the volume ratio of the two phases, which seemed to indicate the presence of impurities. It has now been found that in using 1 ml of aqueous phase and 25 ml of benzene phase the mixing, even at high stirring speeds, is extremely poor. Hence, it takes far longer to reach equilibrium in this case than in the case of 25 ml of each phase. The low extraction coefficients, then, are simply due to equilibrium not having been attained.

More recently it has been found that irreproducible extraction coefficients are still obtained using 25 m. of each phase. Four duplicate experiments were run. The extraction coefficient in two experiments were found to agree very well and remain constant over long periods of stirring, whereas the two others showed a dropping off in extraction coefficient with time, one very greatly. The acid and TTA concentrations are being determined in an attempt to find the cause.

Solubility of Pu (IV)-TTA Chelate in Aqueous Solution.

Measurements are now under way to determine the chelation constants for plutonium (IV) and TTA. The chelation constants can be obtained if the solubility of the plutonium TTA chelate is measured at constant ionic strength in solution having various TTA concentrations. Experiments are now in progress to measure the solubility of the Pu(IV) chelate in 1M $HClO_4$. At the present time only two solubilities, which should be considered as only tentative, have been measured. The solubility of the chelate in pure 1.000 M $HClO_4$ is 2.78×10^{-4} M. It is lowered to 6.45×10^{-8} M when the solution composition is 1.000M $HClO_4$ and 0.03434 M TTA. These two solubilities represent the extremes of the chelate solubility in 1.000 M $HClO_4$.

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Extraction of U(VI) by TTA.

A series of extraction experiments have been carried out to determine the distribution coefficient of uranium (VI) between acidic aqueous solutions and benzene solutions of TTA. A wide range of concentrations has been studied. The absorption spectrum of each phase was determined after equilibrium was attained. The spectra are complicated because of the presence of several absorbing species. The analysis of the data taken is in progress.

Extraction of Lanthanum by TTA.

Lack of reproducibility of sample counting has held up further extractions. Corrective measures were tried, such as filtration, centrifugation of samples prior to pipetting, numerous runs on pipetting (both for just delivery and delivery plus rinse) and all met without success. Ten-fold dilution of the buffer followed (since the largest variance came in the aqueous phase) thereby greatly decreasing the residue on the dried plate and reducing self absorption as well as some variance in geometry. Further attempts to level out couting errors will use larger concentrations of activity and count smaller samples on a lower step to reduce errors of geometry to a minimum.

I_2 - 10_3^- Exchange.

Work was continued on the $I_2 - IO_3^-$ rate of exchange. In the (H^+) range 0.05 M to 1.0 M the plot of log of the rate vs. log (H^+) was found to be non-linear. It is not known presently whether this is due to an actual change in rate law or to a change in the activity coefficients of the reacting ions. It is planned to continue measurements using an ionic strength of 2.0 so that in going from 0.05 M to 1 M $HClO_4$ the proportion of $HClO_4$ to $LiClO_4$ in the solutions will not vary so greatly.

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