DATA

Source	λ considered	P_{Cl_2} mm.	P_{H_2O} mm.	Estimated quanta absorbed	P_{O_2} mm.	Molecules O_2	$\phi \frac{O_2}{\text{quanta}}$
Mazda	Visible	2000	7.2		$<7 \times 10^{-4}$		
	365 mμ			$>0.8 \times 10^{20}$			$<1 \times 10^{-4}$
Hg arc		77	13		$<3 \times 10^{-4}$	$<8 \times 10^{15}$	
	313 mμ			$>1 \times 10^{20}$			$<0.8 \times 10^{-4}$
"Fluorolight"	254 mμ	2000	7.2	$>1 \times 10^{20}$	$<5 \times 10^{-4}$	$<1.3 \times 10^{15}$	$<1.3 \times 10^{-4}$

chemical reaction between chlorine and water vapor, unless the improbable hypothesis is made that all products are completely condensable at liquid air temperature.

MALLINCKRODT CHEMICAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASS.

RECEIVED MAY 13, 1938

COMMUNICATIONS TO THE EDITOR

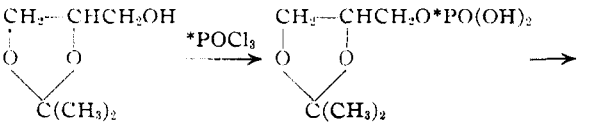
SYNTHESIS OF A RADIOACTIVE ORGANIC COMPOUND: α-GLYCEROPHOSPHORIC ACID

Sir:

The use of radioactive elements as labels in the study of metabolic processes, as initiated by G. Hevesy, already has given highly significant results in a number of cases. Most of the biochemical work accomplished so far has made use of the unstable phosphorus isotope $^{32}_{15}P$. The usual experimental procedure involves the administration to animals of a sodium phosphate solution containing a minute amount of radioactive sodium phosphate and the study of the distribution of the radioactive phosphorus in various organs or chemical fractions isolated from them. While valuable results may be obtained in this manner, it is obvious that the application of organic derivatives of radioactive phosphorus offers even greater possibilities. The development of methods for the synthesis *in vitro* of such compounds is therefore of interest. Biochemical synthesis, while theoretically possible, would be expected to yield products of lower activity and less definitely controllable composition.

For these reasons the synthesis of radioactive phosphorus oxychloride, $*POCl_3$,[1] was carried out, which, as is well known, is an excellent reagent for the introduction of phosphoric acid into organic compounds. The radioactive phosphorus was obtained by the action of fast neutrons liberated by a radon-beryllium source on carbon disulfide. For this material we are indebted to Dr. J. R. Dunning of the Department of Physics of Columbia University. To the reddish residue remaining after the evaporation of the carbon disulfide [*cf.* O. Chievitz and G. Hevesy, *Kgl. Danske Videnskab. Selskab., Biol. Medd.*, **13,** 9 (1937)] a small amount of dry red phosphorus was added and the mixture converted into the chlorides which were sublimed at a pressure of 10^{-5} mm. The sublimate was converted into $*PCl_3$, diluted with ordinary PCl_3 and rectified by distillation. The radioactive PCl_3 obtained was oxidized to $*POCl_3$ by means of potassium chlorate [F. Ullmann and A. Fornaro, *Ber.*, **34,** 2172 (1901)], and the *radioactive phosphorus oxychloride* was purified by fractionation.

With this material the synthesis of *radioactive α-glycerophosphoric acid* was carried out according to E. Fischer and E. Pfähler [*Ber.*, **53,** 1606 (1920)]. The synthesis involved the following steps:



Isopropylidene glycerol

Radioactive isopropylidene α-glycerophosphoric acid

$CH_2(OH)CH(OH)CH_2O*PO(OH)_2$

Radioactive α-glycerophosphoric acid

The barium salts of the radioactive α-glycerophosphoric acid and of its acetone derivative were both obtained in crystalline form, the former

(1) In writing formulas, analytical figures, etc., for compounds containing an unstable isotope it is proposed to express this fact by using an asterisk before the letter symbol for the particular element, *e. g.*, $*I$, $*S$.

crystallizing from hot water as clusters of fine needles (calcd. for $C_3H_7O_6PBa$:P, 10.1; Ba, 44.7; found: P, 9.8; Ba, 44.3).

The radioactivity of the various samples was measured by means of a sensitive Geiger–Müller counter; the substances, in aqueous solution, being contained in a standardized glass cell. This technique, in contrast to the usual method of ignition and measurement of the activity of the ash, makes it possible subsequently to manipulate the radioactive substances unchanged. It leads, however, to considerably lower activity counts than those obtained with the ashed residues. Representative solutions of sodium glycerophosphate and of phosphoric acid (from the phosphorus oxychloride originally employed), containing 84.8 and 70.9 mg. of phosphorus, respectively, yielded respective counts of 0.797 and 0.815 impulses per minute per mg. of phosphorus when examined under strictly comparable conditions. As was to be expected, the ratio $^{32}_{15}P$: $^{31}_{15}P$ was constant in all compounds prepared, after allowance had been made for the natural decay of the unstable isotope.

This work has been made possible by a grant from the John and Mary R. Markle Foundation.

DEPARTMENT OF BIOLOGICAL CHEMISTRY
COLUMBIA UNIVERSITY ERWIN CHARGAFF
NEW YORK, N. Y.

RECEIVED JUNE 4, 1938

THE TRANSIENT INHIBITION OF THE THERMAL DECOMPOSITION OF BUTANE BY NITRIC OXIDE

Sir:

It has been shown by the writers [Echols and Pease, THIS JOURNAL, **59**, 766 (1937)] that the decomposition of butane is inhibited by nitric oxide. Subsequent study of the reaction has clearly indicated that the inhibition by nitric oxide is a *transient effect.* Careful analysis of the reacted gases has shown that this is not the result of removal of the nitric oxide by reaction.

For example, with 200 mm. of butane and 20 mm. of nitric oxide at 520° it is found that the initial slope of the reaction curve is nearly zero, but that the slope slowly rises with time until at 20% reaction it is very nearly that of the uninhibited reaction at the same percentage decomposition. Under these conditions less than 10% of the nitric oxide has reacted.

It has been found that these facts, together with all of the data so far obtained on the phenomenon, may be very nearly quantitatively explained by the assumption that the nitric oxide forms an unstable compound with chain carriers leading to an equilibrium of the form:

$$R + NO \rightleftarrows NOR$$

where R is the chain carrier, presumably a free radical.

This equilibrium is slowly established in the initial stages of the reaction and as the equilibrium is approached the "feed-back" of radicals neutralizes the inhibition, producing a normal rate of the butane decomposition. A detailed discussion of the facts will be presented shortly.

FRICK CHEMICAL LABORATORY L. S. ECHOLS
PRINCETON UNIVERSITY R. N. PEASE
PRINCETON, N. J.

RECEIVED JUNE 20, 1938

THE POSITION OF THE CARBOXYL GROUP IN LYSERGIC ACID

Sir:

We have reported previously [*J. Biol. Chem.*, **113**, 760 (1936)] that dihydrolysergic acid, contrary to lysergic acid which loses carbon dioxide and methylamine somewhat above 200°, can be sublimed at 25 mm. from a bath heated at 300°. [*Anal.* Calcd. for $C_{16}H_{18}O_2N_2$: C, 71.06; H, 6.72. Found: C, 71.3; H, 6.61.] However, more recent investigation of the sublimation of α-dihydrolysergic acid has shown that a chemical change accompanies such sublimation which is accentuated by raising the temperature to 350°. A neutral substance was isolated from the chloroform solution of the sublimate after extraction of dihydrolysergic acid with dilute potash. After recrystallization from methyl alcohol, the substance was obtained in a yield of 33% (m. p. 305–307° with decomposition) $[\alpha]^{25}D - 219°$ (*c*, 0.48 in pyridine). Analysis showed that its formation involved loss of water. [*Anal.* Calcd. for $C_{16}H_{16}ON_2$: C, 76.15; H, 6.40; N, 11.11; $(N)CH_3$, 5.96. Found: C, 76.10; H, 6.58; N, 11.02; CH_3, 5.04.] Contrary to dihydrolysergic acid, it no longer dissolved in dilute acid or alkali, but it still gave the characteristic Keller color reaction unimpaired. Also contrary to the dihydro acid, it was found to be unsaturated since on catalytic hydrogenation it absorbed 1 mole of hydrogen with the formation of a neutral dihydro derivative which melted with decomposition at 336°. [*Anal.* Calcd. for $C_{16}H_{18}ON_2$: C, 75.54; H, 7.14. Found: C, 75.50; H, 7.12.]