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.

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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.

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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) $[\alpha]^{25}\text{D} -219°$ (*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.]