titanium derivatives as catalysts for the low-pressure polymerization of ethylene prompt us to report some related work which we carried out several years ago. In several respects our results differ considerably from theirs.

An orange solution of bis-(cyclopentadienyl)-titanium dichloride in toluene (5 millimoles per liter) was treated with two moles of diethylaluminum chloride. The color immediately changed to a dark red, followed by a gradual change over a period of about an hour at room temperature to a green and finally to a blue solution. During this time ethane was evolved. (With triethylaluminum the formation of the blue solution was practically instantaneous; the slow reaction reported by Natta can be attributed to the insolubility of the dichloride in heptane.) Replacement of the toluene by *n*-heptane yielded a clear blue solution, from which a blue crystalline solid could be isolated by chilling in Dry Ice. After several recrystallizations it melted at 80–90°, apparently with some decomposition. Although the compound seemed to be thermally stable at room temperature, it was extremely sensitive to traces of oxygen. The compound is a complex of $(C_5H_5)_2Ti(III)Cl$ with what appears to be aluminum sesquichloride. *Anal.* Calcd. for $(C_5H_5)_2TiCl\cdot{}^1/_2(C_2H_5)_2AlCl\cdot{}^1/_2C_2H_5AlCl_2$: C, 46.28; H, 5.23. Found: C, 46.36; H, 5.26. Analysis of a heptane solution gave the ratios (normalized for total titanium) Ti(III or less), 0.95; Al, 1.05; Cl, 2.63. Magnetic susceptibility measurements showed the presence of one unpaired electron, while hydrolysis with thoroughly deaerated dilute mineral acid gave a green aqueous solution; the $(C_5H_5)_2Ti(III)$ ion is reported to be green.[3] There seems to be little doubt that, by analogy, the compound isolated by us and by Natta and co-workers from bis-(cyclopentadienyl)-titanium dichloride and triethylaluminum has the structure $(C_5H_5)_2TiCl\cdot(C_2H_5)_2AlCl$, the "sandwich" compound reacting with alkylaluminum compounds in a manner similar to titanium tetrachloride.

The blue complex prepared with diethylaluminum chloride is a very poor catalyst for the polymerization of ethylene, in agreement with the observations of Natta and co-workers on the complex prepared with triethylaluminum. A fresh mixture of bis-(cyclopentadienyl)-titanium dichloride and diethylaluminum chloride, however, is a highly active catalyst, as is the blue complex if the ethylene contains a trace of oxygen.[4] The color changes in the latter case indicate quite definitely that the oxygen is functioning to form a tetravalent titanium compound. Thus, ethylene containing 0.003 mole % oxygen was passed into a solution of 5 millimoles of bis-(cyclopentadienyl)-titanium dichloride and 10 millimoles of diethylaluminum chloride in a liter of toluene at 15–20°. The blue solution turned green, and 13 g. of polyethylene was formed in one hour. Under the same conditions ethylene containing 0.025% oxygen gave a brown solution; the addition of small amounts of a dilute solution of diethylaluminum chloride to maintain this color during the polymerization resulted in the formation of 174 g. of polyethylene in one hour. Thus, these catalysts are fully as active as the usual Ziegler type. There seems to be little doubt from these results that this *soluble* catalyst system depends for its catalytic activity on the presence of at least some tetravalent titanium. The polymers differ from polyethylene prepared with the usual Ziegler-type catalysts in being more linear (methyl content about 0.05% *vs.* about 0.9%) and higher melting (137° *vs.* 132°).

(3) G. Wilkinson and J. M. Birmingham, THIS JOURNAL, **76**, 4281 (1954).

(4) D. S. Breslow, Belgian Patent 551,283 (1957).

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INHIBITION BY HYDROGEN PEROXIDE OF THE SECOND EXPLOSION LIMIT IN HYDROGEN–OXYGEN MIXTURES

Sir:

During a recent investigation of the gas-phase decomposition of hydrogen peroxide[1] in which we confirmed the partially homogeneous character of the reaction above 400°, we tried adding a number of gases to study their effect on the rate of peroxide decomposition. Of the various gases tested (H_2, O_2, NO, etc.) only hydrogen showed significant effects: a marked acceleration of the reaction in the temperature range 440–470° at total pressures in excess of 20 mm., in agreement with the findings of McLane[2] in a flow system. At lower pressures we observed explosive reactions of the hydrogen with the oxygen from decomposition of the peroxide. However, a remarkable feature of these explosions was that they occurred only after all, or nearly all, the hydrogen peroxide had disappeared although the mixtures were within the explosion range[3] for some time yet. This pointed out to a strong inhibiting action of hydrogen peroxide apparently not reported before.

To check this point further we added some hydrogen peroxide vapor to stoichiometric hydrogen–oxygen mixtures and determined the second limit by the usual withdrawal method. The preliminary results confirm, indeed, that hydrogen peroxide is an efficient explosion inhibitor, roughly ten times as efficient as water vapor under the same conditions. For instance at 458° the second limit was lowered from 28 mm. to 17 mm. by about 0.01 mole per cent. of hydrogen peroxide, while at 0.04 mole per cent., the explosions were suppressed entirely. There is some uncertainty in our results as to the exact concentration of peroxide at the moment of explosion because its decomposition rate depends on such continuously changing variables as total pressure and concentration of hydrogen gas in the system. Water vapor from the decomposing peroxide also acts as an inhibitor, but this is of minor importance in our case. That the above phenomenon has not been noticed previously is no doubt due to the fact that, unless special care is exercised, hydrogen peroxide will decompose quickly through a heterogeneous mechanism before the necessary

(1) P. A. Giguère and I. D. Liu, *Can. J. Chem.*, **35**, 283 (1957).

(2) C. K. McLane, *J. Chem. Phys.*, **18**, 972 (1950).

(3) B. Lewis and G. von Elbe, "Combustion, Flames and Explosions," Academic Press, Inc., New York, N. Y., 1951.

high temperature is reached. Using specially treated 2-liter Pyrex or Vycor flasks we succeeded in reducing the extent of surface decomposition enough to follow the over-all reaction up to 600° at low pressures.[1] The present results are too scanty for an adequate discussion of possible mechanisms although certain chain-breaking processes immediately come to mind.

We have also confirmed the observation of McLane[2] regarding the catalytic action of hydrogen peroxide on the slow hydrogen-oxygen reaction above the second limit; under certain conditions there were indications of rapid self-heating of the mixture prior to explosion and, in other cases, of slow pressure decrease afterward, as in "afterburning." All these effects are being investigated systematically and the results will be published elsewhere.

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DEOXYCYTIDINE DIPHOSPHATE CHOLINE, A NEW DEOXYRIBOSIDIC COMPOUND

Sir:

Our previous report[1] described the presence of "masked" deoxyribosidic compounds in the acid soluble extracts of sea urchin eggs and several other tissues including microörganisms and mammalian viscera. The present communication deals with the further characterization of one of the "masked" deoxyribosidic compounds of sea urchin eggs, which has now been identified as deoxycytidine diphosphate choline, a new deoxynucleotide derivative.

The acid soluble deoxyribosidic compounds were chromatographed on a column of Dowex-1 (X-2, formate) as previously described.[1] The fraction under consideration eluted by 0.1*M* AM-F[2] (*p*H 4.5) (Fraction No. 5 of the previous report) was rechromatographed on the same resin, employing formic acid as an eluent, and the fractions having a CMP-like spectrum were pooled, neutralized, and again applied to a column of Dowex-1 (X-8, formate). The column was then eluted by gradient elution with AM-F (*p*H 7.8) containing sodium tetraborate to yield two separate fractions, designated F_1 and F_2, both having a spectrum similar to CMP. In this system, F_1 was eluted slightly faster than F_2 and the both emerged from the column much more rapidly than authentic deoxy-CMP and CMP. They were further purified by paper chromatography (solvent system 0.02 *N* acetic acid in 60% ethanol[3]), and analyzed for their base, deoxyriboside, phosphorus and choline contents (Table I).

Only after the venom digestion[1] does F_1 become active toward *Lactobacillus acidophilus* R-26, the deoxyriboside requiring organism.[5] Hydrolysis of F_1 and F_2 with 1 *N* HCl for 15 minutes at 100°, followed by paper chromatography yielded deoxy-CMP and CMP, respectively. After the venom digestion, F_1 gave deoxycytidine and choline, F_2 cytidine and choline, identified by paper chromatography. The presence of choline residues in F_1 and F_2 is in harmony with the fact that, in anion exchange chromatography at *p*H 7.8, F_1 and F_2 behaved less anionic than deoxy-CMP and CMP in spite of their high phosphorus contents (Table I). In the microbiological determination of choline, it was noticed that F_1 as well as F_2 did not support the growth of a choline-less mutant of *Neurospora* until after digestion with snake venom, the situation being very similar to that seen in the microbiological determination of deoxyriboside of F_1.

TABLE I

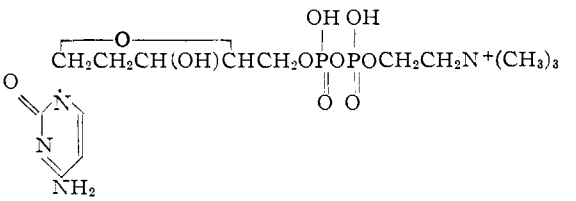
ANALYTICAL DATA OF F_1 AND F_2

	μmole/μmole deoxycytidine or cytidine[a]				
	Deoxyriboside[b] Venom treatment		Phosphorus[c]	Choline[d] Venom treatment	
	Before	After		Before	After
F_1	0.15	0.93	1.93	0	0.83
F_2	0	0	2.03	0	0.87

[a] Deoxycytidine or cytidine moiety identified by characteristic ultraviolet spectrum in acid and alkali. Estimated from 260 mμ absorption at *p*H 2 using $\epsilon = 6200$.[4] [b] Determined microbiologically.[5] Venom treatment was the same as that previously described.[1] [c] Determined by the method of Fiske–SubbaRow.[6] [d] Determined microbiologically.[7] Venom treatment was the same as that used for deoxyriboside determination.[1]

The action of snake venom, which results in the liberation of deoxycytidine and choline, can be attributed to its nucleotide pyrophosphatase and 5′-nucleotidase activity. This view coincides well with the recent report of Schneider and Potter,[8] who demonstrated that di- or triphosphates of pyrimidine deoxyribosides do not support growth of *L. acidophilus* R-26 unless they are dephosphorylated to monophosphates by acid hydrolysis.

From the analytical data shown in Table I and several other lines of evidence mentioned above, it is concluded that F_1 is deoxycytidine diphosphate choline



and F_2 cytidine diphosphate choline, which was discovered previously by Kennedy and Weiss.[3,9]

Recently, Potter[10] reported the occurrence of similar compounds in calf thymus and described

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(2) The following abbreviations are used: AM-F = ammonium formate, CMP = cytidylic acid, CDP = cytidine diphosphate.

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(5) E. Hoff-Jørgensen, *Biochem. J.*, **50**, 400 (1952); "Recent Developments in Cell Physiology" (edited by J. A. Kitching), Butterworth Scient. Publ., London, 1954, pp. 79–90.

(6) C. H. Fiske and Y. SubbaRow, *J. Biol. Chem.*, **66**, 375 (1925).

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(8) W. C. Schneider and R. L. Potter, *Proc. Soc. Expt. Biol. Med.*, **94**, 798 (1957).

(9) E. P. Kennedy and S. M. Weiss, THIS JOURNAL, **77**, 250 (1955); *Federation Proc.*, **14**, 234 (1955).

(10) R. L. Potter and V. Buettner-Janusch, *ibid.*, **16**, 234 (1957).