shown in the accompanying diagram. It consists essentially of two concentric tubes and the cooling is produced by the circulation of pre-cooled nitrogen. The design is after a suggestion of Dr. F. Simon.

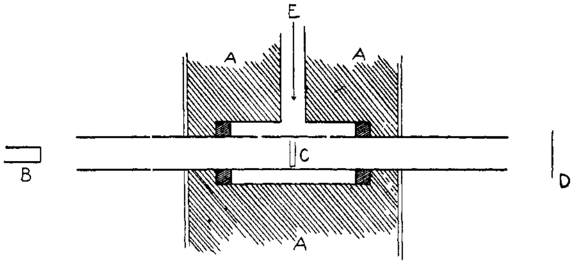

Fig. 1.—A, Lagging (cotton waste); B, hydrogen discharge tube; C, pepsin; D, spectrograph; E, pre-cooled nitrogen.

Further details will be published shortly.

FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY
AND THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH
PRINCETON, N. J.
G. I. LAVIN
J. H. NORTHROP
H. S. TAYLOR

RECEIVED JUNE 21, 1933 PUBLISHED AUGUST 5, 1933

THE REACTION BETWEEN ATOMIC HYDROGEN AND CARBON TETRACHLORIDE

Sir:

Previous studies on the reactions of atomic hydrogen with organic compounds have not yielded information about the mechanisms of these changes, due to the complexity of the products and to the large number of consecutive reactions taking place. In a recent series of experiments, it has been found that the reaction between atomic hydrogen and carbon tetrachloride vapor leads to the formation of relatively simple products in addition to the high polymers usually found.

The apparatus is of the conventional type: carbon tetrachloride vapor is admitted to a stream of atomic hydrogen drawn from a Wood discharge tube, the pressure in the reaction zone being maintained at about 0.7 mm. The volatile products of the reaction, together with the unchanged carbon tetrachloride, are frozen out in a liquid air trap.

That extensive reaction takes place is shown by the heat evolved in the reaction zone, the presence of considerable hydrogen chloride in the liquid air trap, the deposition of a solid product on the walls of the reaction chamber, and, if the pressure is sufficiently low, a moderately intense greenish-blue luminescence, appearing at the region of mixing. The solid product is soluble in carbon tetrachloride, but decomposes without melting slightly below red heat. It contains about 55% chlorine and does not decolorize bromine water. The liquid air condensate is mostly carbon tetrachloride and hydrogen chloride. Tests for chloroform and for phosgene were negative. A brown oily residue remained after distillation of the carbon tetrachloride.

The most striking result, however, is the presence in the condensate of a small amount of a volatile substance, which explodes on coming in contact with the air. If, at the conclusion of a run, the contents of the trap are rapidly melted in air, the boiling off of the hydrogen chloride is attended by small repeated explosions. In some of the runs the condensate was covered with water immediately upon removal of the liquid air. Upon warming, the hydrogen chloride passed into the water layer and the explosive substance remained in solution in the carbon tetrachloride. This was evidenced by the fact that the first few drops of distillate from the latter layer exploded on forming in the condenser. These explosions were accompanied by the deposition of a considerable amount of soot.

It seems most plausible to assume that the initial reaction is $CCl_4 + H = CCl_3 + HCl$. The solid product is evidently formed by the association of the CCl_3 fragments and subsequent dechlorination by atomic hydrogen, the removal of chlorine being followed by polymerization. The dechlorination must take place, at least in part, after the material has condensed on the walls. The explosive substance has not been identified. Professor Kohler has pointed out that it might be either mono- or dichloroacetylene. The work will be continued with the objects of establishing the identity of this substance and of deducing the mechanism of its formation.

HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS
HUGH F. SMYSER
HUGH M. SMALLWOOD

RECEIVED JUNE 29, 1933 PUBLISHED AUGUST 5, 1933

THE FORMATION OF METHYL RADICALS IN THE DECOMPOSITION OF AZOMETHANE

Sir:

The formation of the observed products in the homogeneous thermal decompositions of the two unsymmetrical azo compounds, methylisopropyl diimide and dimethyltriazene, is best explained by the assumption that the azo compounds liberate radicals on decomposition and that these radicals later combine at random. In some recently completed work which concerned itself with the possibility that short reaction chains accompany the unimolecular decomposition of azomethane, it was assumed that methyl radicals were formed in that decomposition. In order to avoid ambiguity in the conclusions drawn from the experiments, it was thought advisable to obtain more direct evidence that methyl radicals are actually liberated when azomethane decomposes.

Azomethane was decomposed in an apparatus similar to that described