FREE PHENYL RADICALS IN THE GAS PHASE

Sir:

In the past few years a number of investigators have demonstrated the existence of active gaseous hydrocarbon molecules in experiments in which various types of substances were thermally decomposed. These have been called free radicals. So far only the methyl and ethyl radicals have been reported. In some experiments which we have been performing we have strong indications of the existence of the free phenyl radical in the gas phase.

The apparatus was made of quartz and consisted of a chamber to contain the lead tetraphenyl, a short region inside an electric furnace inclined slightly from the horizontal, a chamber to retain the liquid and crystalline products formed (chiefly diphenyl) and a chamber in which mercury was kept refluxing. The procedure was similar to that used in our work on the chemical reactions of gaseous methyl and ethyl [THIS JOURNAL, 55, 2696 (1933)]. The lead tetraphenyl was kept just below its melting point (215-220°) and the apparatus run for six hours at an indicated pressure of 0.01 mm.

The deposit formed in the mercury reflux chamber was recrystallized from alcohol. Among the characteristic broad crystals of diphenyl there appeared scattered needle-like crystals. Several were picked out and an attempt made to determine their melting point. This was in the region of 120° as near as could be determined with this small sample. The melting point of mercury diphenyl is 120° . A qualitative analysis showed mercury.

As neither lead tetraphenyl nor diphenyl reacts with mercury vapor, we believe that active phenyl radicals were present. Further work is in progress on this problem.

DEPARTMENT OF CHEMISTRY DEPAUL UNIVERSITY, CHICAGO RECEIVED AUGUST 16, 1933 PUBLISHED SEPTEMBER 5, 1933

THE FORMATION OF FREE RADICALS FROM ALIPHATIC AZO COMPOUNDS Sir:

In view of the publication of a communication on this subject by Leermakers [THIS JOURNAL, 55, 3499 (1933)] it seems desirable to publish an account of some work we performed in this connection in August, 1931. We found that both azomethane and azoisopropane readily remove antimony mirrors when passed through a furnace heated in the range 450- 550° ; acetone was used as the carrier gas. The temperature of the furnace was far too low to cause any perceptible decomposition of the acetone.

At that time we were more particularly interested in azoisopropane